Qualitative Chemical Analysis

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FRANK X. MOERK

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QUALITATIVE CHEMICAL ANALYSIS

BY

FRANK X. MOERK

Professor of Analytical Chemistry in the Philadelphia
College of Pharmacy

1905

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Preface.

This little volume is written for the students of the Philadelphia College of Pharmacy and is intended to be used in connection with the lectures and quizzes on laboratory work.

One of the valuable features is the presentation of much of the subject-matter in tabular form, which enables a rapid selection of the desired information.

A very important part of a chemical education, which is too often neglected because its importance is not soon enough realized by the student, is that preliminary part which has for its foundation Valence and the Electro-Chemical Character of the Elements.

The writing of equations must necessarily follow the writing of formulas, and it is generally at this stage that the student discovers that the preliminary part was neglected either through faults of his own or of his instructors. The equations are presented under suitable headings, which will materially assist in understanding them.

An outline or classification of the observations which are utilized in the course of analysis is given as an introductory to Analytical Chemistry proper, and this is then followed by the tests for metals in tabular arrangement. The student in making these tests knows that something will happen, but what, he does not know until the test is actually made; this method prevents the student from railroading the tests, which is considered by most students a mechanical achievement, but the results impress him for a short time only. By requiring the student to submit the results of these tests for inspection, he is taught to cultivate his powers of observation.

Tests for the Acids are also arranged in tabular form, and the Scheme for the Detection of Acids which follows aims to avoid, as far as it is possible to do so, the incompatibilities and interferences of acids with each other.

In connection with the tests for Simple Solids an illustrative table is given, a study of which should show the student the importance of making some preliminary tests and, taking advantage of these by a proper interpretation, avoid making many unnecessary tests.

The analysis of urine, because of its importance to the pharmacist, has been given careful consideration and attention is called in the various tests to the interferences caused by the administration of drugs.

The preparation and strength of the Reagents used throughout the text are furnished as a concluding part.

PHILADELPHIA, December 8, 1904.

FRANK X. MOERK.

Table of Contents.

PRELIMINARY CHEMICAL CONSIDERATIONS:
- Simple Molecules 1
- Tables of Symbols, Atomic Weights, Valences and Electro-chemical Position of the Elements 2, 3
- Compound Molecules 4, 5
- List of Important Acids 5
- Exercises in Writing Formulas and Names of Compound Molecules 6, 7

CHEMICAL CHANGES OR REACTIONS:
- Physical Reagents 7
- General Underlying Law 7
- Laws Governing Exceptions 7

CLASSIFICATION OF REACTIONS:
- Direct Union 8
- Double Decomposition 8
- Elements upon Compound Molecules . . 9
- Oxidation and Reduction 9–12
- Decompositions by Heat 12

PHYSICAL PROPERTIES UTILIZED IN CHEMICAL ANALYSIS:
- Classification 13
- Solubility and Stability of Chemical Compounds 13–15
- Test-Papers 16
- Production of Colored Solutions 16
- Flame Tests 16
- Borax Beads 17
- Colored Residues on Porcelain 17
- Colored Incrustations on Charcoal . . . 17
- Formation of Gaseous or Volatile Substances 17, 18

ANALYTICAL CHEMISTRY:
- Strength of Unknowns 18

TESTS FOR METALS OR BASES:
- Color of Solutions Due to Metals 18
- Table of Tests 19
- Action of Group Reagents 20
- Analytical Operations 20, 21
- Notes on the Scheme for Separation of Bases 21–26
- Notes on the Phosphate Chart 26–27
- Analysis of Solutions Containing only Part of the Groups 27
- Short Processes in Absence of some Metals, 27
- Scheme for the Separation of Bases . 28–30
- Phosphate Chart 31
- Direct Tests for Metals in Solutions . 32–33

TESTS FOR ACIDS:
- More Important Precipitants 33
- Special Behavior of Some Acids 33
- Table of Tests 34
- Scheme for the Detection of Acids . . 35–39

NOTES ON TESTING FOR BASES AND ACIDS:
- Solutions 40
- Simple Solids 40–43
- Table of Behavior of Typical Simple Solids 42
- Mixed Solids 43
- Alloys 43

URINALYSIS:
- Normal Urine 44
- Abnormal Urine 44
- Volume, Color, Reaction 44
- Odor, Transparency 44
- Specific Gravity, Total Solids 44, 45

TESTS FOR:
- Albumin 45
- Peptones 46
- Sugar (Dextrose) 46, 47
- Aceto-acetic Acid 47
- Hydroxy-butyric Acid 47
- Acetone 48
- Urea 48
- Uric Acid 48
- Urinary Pigments 48
- Biliary Pigments 49
- Blood Pigments 49
- Pus 49

DIAZO-REACTION 50

URINARY CONCRETIONS 50

URINARY SEDIMENTS 50

REAGENTS:
- Preparation and Strength 51–53

ERRATA 53

Preliminary Chemical Considerations.

The study of Analytical Chemistry requires of the student the ability to write correctly the formulas of the substances used in the tests or experiments, which, supplemented by the knowledge of a few general laws governing chemical changes, will enable the understanding of the reactions or changes taking place in the tests or experiments.

This requisite fundamental knowledge consists in a proper appreciation of the influence of the position of the elements in the Electro-Chemical Series and the application of the Valences of the Atoms in the writing of formulas of Compound Molecules, starting with the formulas of Binary Molecules, and gradually leading up to the more complicated Ternary Molecules.

The Electro-Chemical Series is so arranged that any element is *electro-negative* to all other elements below it, and *electro-positive* to all elements above it. The chemical elements are divided into two large classes, the *electro-negative* and the *electro-positive;* of these members of the former class unite with each other to form numerous Binary Molecules, in which one of the two elements acts as the negative, and the other *must* act as the positive element; the members of the electro-positive class of elements do not combine with each other, but numerous important reactions take place because a weaker electro-positive element is displaced from combination by a stronger electro-positive element. This latter statement also applies to electro-negative elements.

The position of the elements in the Electro-Chemical Series also decides the question of *variation* in *valence* (the combining or replacing power of an atom expressed in Hydrogen units); thus the atom constituting the *electro-negative* part of a compound molecule always has a *fixed valence*, but when the same atom acts as the *electro-positive* part of a compound molecule it displays its *maximum variation in valence.*

Simple Matter, or the **Chemical Elements** or **Atoms** are conveniently divided into

1. NON-METALS, ELECTRO-NEGATIVE, or generally ACID-FORMING ELEMENTS.
2. METALS, ELECTRO-POSITIVE, or generally BASE-FORMING ELEMENTS. As a rule two like atoms make up the **Simple** or **Elemental Molecule** (diatomic), which is capable of existing in the free state; the important exceptions are Ba, Cd, Hg, Zn (monatomic); O as ozone (triatomic); As, P (tetratomic).

Table of Non-Metals.

Electro-Chemical Position of Non-metals.	Symbols.	Atomic Weights.		VALENCES.					
Negative End.		H = 1	O = 16		When Negative.	When Positive (or Acid-forming).			
Oxygen . . .	O	15·88	16·00	**F**	I			I	
Sulphur . . .	S	31·83	32·06	**Cl**	I	I	III	V	VII
Nitrogen . . .	N	13·93	14·04	**Br**	I	I	III	V	VII
Fluorine . . .	F	18·90	19·00	**I**	I	I	III	V	VII
Chlorine . . .	Cl	35·18	35·45	**O**	II*	——	——	——	——
Bromine . . .	Br	79·36	79·96	**S**	II	II	IV	VI‡	$(S_2)^{\text{XIV}}$
Iodine	I	125·90	126·85	**Se**	II	II	IV	VI	
Selenium . . .	Se	78·60	79·20	**Te**	II	II	IV	VI	
Phosphorus .	P	30·77	31·00	**W**			IV	VI	
Arsenic . . .	As	74·40	75·00	**B**	III			III	
Vanadium . .	Va	50·80	51·20	**N**	III	I	III†	V§	
Tungsten . .	W	182·60	184·00	**Va**		I	III	V	
Boron	B	10·90	11·00	**P**	III		III	V‖	
Carbon	C	11·91	12·00	**As**	III		III	V	
Tellurium . .	Te	126·60	127·60	**Si**	IV			IV	
Titanium . . .	Ti	47·70	48·10	**C**	IV		II	IV¶	
Silicon . . .	Si	28·20	28·40	**Ti**			II	$(Ti_2)^{\text{VI}}$IV	
Metals	Characteristic Terms:								
	For Binaries				ide	Hypo—ous	—ous	—ic	Per—ic
	For Ternaries: (1) Acids . . .					Hypo—ous	—ous	—ic	Per—ic
	(2) Salts . . .					Hypo—ite	—ite	—ate	Per—ate
Positive End.									

* $(OH)^{\text{I}}$ Hydroxyl.
† $(NO)^{\text{I}}$ Nitrosyl.
‡ $(SO_2)^{\text{II}}$ Sulphuryl.
§ $(NO_2)^{\text{I}}$ Nitroxyl.
‖ $(PO)^{\text{III}}$ Phosphoryl.
¶ $(CO)^{\text{II}}$ Carbonyl; $(CN)^{\text{I}}$ Cyanogen.

Table of Metals.

Electro-Chemical Position of Metals. Negative End. Non-metals.	Symbols.	Atomic Weights.		VALENCES.				
		H = 1	O = 16		Base-forming.		Acid-forming.	
Hydrogen	H	1·00	1·008	**H**		I		
Gold	Au	195·70	197·20	**K**		I		
Platinum	Pt	193·30	194·80	**Na**		I		
Silver	Ag	107·12	107·93	**Li**		I		
Mercury	Hg	198·50	200·00	**(NH_4)**		I		
Antimony	Sb	119·30	120·20	**Ag**		I		
Bismuth	Bi	206·90	208·50	**Mg**		II		
Copper	Cu	63·10	63·60	**Zn**		II		
Lead	Pb	205·35	206·90	**Cd**		II		
Molybdenum	Mo	95·30	96·00	**Hg**	$(Hg_2)^{II}$	Hg^{II}		
Nickel	Ni	58·30	58·70	**Cu**	$(Cu_2)^{II}$	Cu^{II}		
Cobalt	Co	58·56	59·00	**Ba**		II (IV)		
Tin	Sn	118·10	119·00	**Sr**		II (IV)		
Uranium	U	236·70	238·50	**Ca**		II (IV)		
Chromium	Cr	51·70	52·10	**Pb**		II (IV)		
Cadmium	Cd	111·60	112·40	**Sn**	II	IV		
Cerium	Ce	139·20	140·25	**Pt**	II	IV		
Iron	Fe	55·50	55·90	**Co**	II	$((Co_2)^{VI})$		
Manganese	Mn	54·60	55·00	**Ni**	II	$((Ni_2)^{VI})$		
Zinc	Zn	64·90	65·40	**Fe**	II	[IV] $(Fe_2)^{VI}$	VI	
Aluminum	Al	26·90	27·10	**Mo**	II	[IV] $(Mo_2)^{VI}$	VI	
Magnesium	Mg	24·18	24·36	**Cr**	II	$(Cr_2)^{VI}$	VI§	$(Cr_2)^{XIV}$
Calcium	Ca	39·80	40·10	**Mn**	II	(IV) $((Mn_2)^{VI})$	VI	$(Mn_2)^{XIV}$
Strontium	Sr	86·94	87·60	**Au**	I	III		
Barium	Ba	136·40	137·40	**Sb**	III*	V		
Lithium	Li	6·98	7·03	**Bi**	III†	V		
(Ammonium)	NH_4	17·93	18·07	**Al**		$(Al_2)^{VI}$		
Sodium	Na	22·88	23·05	**Ce**	$(Ce_2)^{VI}$	(Ce^{IV})		
Potassium	K	38·86	39·15	**U**	IV	VI‡		
		Characteristic Terms:						
		For Binaries			—ous	—ic	—ic	Per—ic
		For Ternaries:						
Positive End.		(1) Bases			—ous	—ic	——	——
		(2) Acids			——	——	—ic	Per—ic
		(3) Salts			—ous	—ic	—ate	Per—ate

Valences enclosed in parentheses (   ) to be used with **O** and **(OH)** only.
Valences enclosed in brackets [   ] to be used with **S** only.

* $(SbO)^{i}$ Antimonyl.
† $(BiO)^{i}$ Bismuthyl.
‡ $(UO_2)^{ii}$ Uranyl.
§ $(CrO_2)^{ii}$ Chromyl.

Compound Matter or **Compound Molecules** are composed of unlike atoms, combined according to valence.

1. **Binary Molecules** composed of two kinds of atoms, directly united according to valence. Of these the *Haloid Acids* (compounds of F, Cl, Br, I with H) and *Haloid Salts* (produced by union of the Haloid Acids with bases) form special groups.
2. **Ternary Molecules** composed usually of three kinds of atoms, two of which are indirectly united by the aid of the third. O as the most important linking element is considered in the following statements (S, N and a few other elements also possess this property).

    a. BASES or METALLIC HYDRATES are the compounds of the metals with $(OH)^1$; their formulas are written by placing the symbol of the metal first, followed by the proper number of (OH) groups; the number of (OH) groups constitutes the acidity of the bases expressed as mon-acid, di-acid, etc., etc. The (OH) is as a rule firmly combined, but in the case of Au, Pt, Ag, Hg and Sb the hydrates are unknown, and in the case of Cu, Bi, Mn and Fe there is a tendency to lose part or all of the combined H_2O with the formation of oxides or oxy-hydrates.

    b. ACIDS or NON-METALLIC HYDRATES are the compounds of non-metals (and a few metals in their higher valences) with (OH); in writing their formulas, the H is placed first, then the acid-forming element, and lastly the O. Written in this manner the number of H atoms constitutes, with few exceptions, the basicity of the acids, expressed as mono-basic, di-basic, etc., etc. For list of important acids see opposite page.

    aa. *Ortho-acids*, constituted as above explained, contain an equal number of H and O atoms.

    bb. *Meta-acids* result from the ortho-acids (containing three or more (OH) groups) by the loss of one or more molecules of H_2O; every molecule of H_2O split off must affect two (OH) groups, leaving one atom of O, which takes the place of the two (OH) groups in saturating the valence of the acid-forming element. Therefore, in all normally constituted meta-acids, the number of O atoms must exceed that of the H atoms, and the difference between the two equals the number of molecules of water which has split off from the formula of the ortho-acid. In some cases two or even more molecules of ortho-acid (or meta-acids) are affected by this loss of H_2O, resulting in the formation of meta-acids containing more than one atom of the acid-forming element; these acids are generally named by using a numeral prefix to indicate the number of acid-forming atoms, or in some cases by using the prefix *pyro*.

    If elimination of H_2O removes all of the H, a Binary Molecule results, which is an *oxide* or *acid anhydride*.

    cc. *Haloid Acids* are Binary Molecules, containing no O.

    c. SALTS are produced by the union (neutralization) of bases and acids, with the elimination of H_2O, which is best considered as being formed from the (OH) of the base and the H of the acid.

    aa. *Normal Salts* contain neither (OH) from the base nor H from the acid, both base and acid being perfectly neutralized; they are possible from any base and acid by taking a sufficient number of molecules of each to equalize the OH and H.

    bb. *Basic Salts* are possible whenever the number of (OH) groups in the formula of the base exceed the replaceable H atoms of the acid, thus enabling but a partial neutralization of the base; characteristic of this class is the residual (OH) from the base, or O in case two residual (OH) groups have split off H_2O, which allows them to unite with more acid to form normal salts.

cc. Acid Salts are possible whenever the number of replaceable H atoms of the acid exceed the number of (OH) in the formula of the base, thus enabling but a partial neutralization of the acid; characteristic of this class is the residual H from the acid, which allows them to unite with more base to form normal salts.

dd. Double Salts contain at least two kinds of positive elements, replacing the H atoms from either one molecule of a polybasic acid, or from several molecules of the respective acid. They are not possible from all bases and acids, so that when they are formed it indicates some special preference between the respective bases and acid.

ee. Haloid Salts are Binary Molecules.

List of the More Important Acids.

INORGANIC.

Arsenous	H_3AsO_3	Hypoiodous	HIO
Metarsenic	$HAsO_3$	Hypophosphorous	$H(H_2PO_2)$
(Ortho-)arsenic	H_3AsO_4	Hyposulphurous (Hydrosulphurous)	H_2SO_2
Pyro-arsenic	$H_4As_2O_7$	Manganic	H_2MnO_4
Meta-boric	HBO_2	Molybdic	H_2MoO_4
(Ortho-)boric	H_3BO_3	Nitric	HNO_3
Tetra-boric (Pyroboric)	$H_2B_4O_7$	Nitrous	HNO_2
Bromic	$HBrO_3$	Permanganic	$H_2Mn_2O_8$
Carbonic	H_2CO_3	Persulphuric	$H_2S_2O_8$
Chloric	$HClO_3$	Meta-phosphoric	HPO_3
Chromic	H_2CrO_4	(Ortho-)phosphoric	H_3PO_4
Di-chromic	$H_2Cr_2O_7$	Pyro-phosphoric	$H_4P_2O_7$
Hydriodic	HI	Phosphorous	$H_2(HPO_3)$
Hydrobromic	HBr	Ortho-silicic	H_4SiO_4
Hydrochloric	HCl	(Meta-)silicic	H_2SiO_3
Hydrofluoric	HF	Sulphuric	H_2SO_4
Hydrosulphuric (Hydrogen sulphide)	H_2S	Disulphuric (Pyrosulphuric)	$H_2S_2O_7$
Hypobromous	$HBrO$	Sulphurous	H_2SO_3
Hypochlorous	$HClO$	Thiosulphuric (Hyposulphurous)	$H_2S_2O_3$

ORGANIC.

Acetic	$H\overline{A}$	$HC_2H_3O_2$	Oleic	$H\overline{Ol}$	$HC_{18}H_{33}O_2$
Benzoic	$H\overline{Benz}$	$HC_7H_5O_2$	Palmitic	$H\overline{Pal}$	$HC_{16}H_{31}O_2$
Citric	$H_3\overline{C}$	$H_3C_6H_5O_7$	Salicylic	$H\overline{Sal}$	$HC_7H_5O_3$
Formic	$H\overline{F}$	$HCHO_2$	Stearic	$H\overline{St}$	$HC_{18}H_{35}O_2$
Gallic	$H\overline{Gal}$	$HC_7H_5O_5$	Succinic	$H_2\overline{Suc}$	$H_2C_4H_4O_4$
Hydrocyanic	HCy	HCN	Sulphocarbolic	——	$C_6H_4(OH)HSO_3$
Hydroferricyanic	$H_6\overline{Cfy}_2$	$H_6Fe_2(CN)_{12}$	Sulpho-cyanic	$HCyS$	$HCNS$
Hydroferrocyanic	$H_4\overline{Cfy}$	$H_4Fe(CN)_6$	Tannic	$H\overline{Tan}$	$HC_{14}H_9O_9$
Lactic	$H\overline{Lac}$	$HC_3H_5O_3$	Tartaric	$H_2\overline{T}$	$H_2C_4H_4O_6$
Malic	$H_2\overline{Mal}$	$H_2C_4H_4O_5$	Valerianic	$H\overline{Val}$	$HC_5H_9O_2$

Exercises in Writing Formulas and Names of Compound Molecules.

Binary Molecules.

(1) H and the Non-metals. (2) O and the Non-metals.

(3) Cl and the Metals. (4) O and the Metals.

Ternary Molecules.

(5) (OH) and the Metals. (6) (OH) and the Non-metals.

(7) Change Ortho-acids into Meta-acids by splitting off H_2O.

(8) Write formulas and names of all the Normal salts and, whenever possible, of the Acid or Basic salts from the following bases and acids:
a. $NaOH$; **b.** $Ca(OH)_2$; **c.** $Bi(OH)_3$; **d.** $Fe_2(OH)_6$.
e. HNO_3; **f.** H_2SO_4; **g.** H_3PO_4; **h.** $H_4P_2O_7$.

These exercises will impress upon the student the following facts:

In (1) that H is positive towards all of the Non-metals, and that the latter act with but a single valence.

In (2) that O is negative and the other Non-metals are positive, which accounts for the variation in valence, whenever possible.

In (3) that Cl is negative, the metals positive; the former acts only with the valence I; the latter may vary, but only those base-forming valences must be used which are not enclosed in parentheses. If the enclosed valences or those titled acid-forming be used, the result in practice will be that Cl is split off and a compound of the metal with a lower valence produced.

In (4) that *all* valences (excepting those in brackets, characteristic of S) are to be used.

In (5) use same valences as in (4) and note that the compounds produced are *bases*, excepting a few higher valences which yield *acids*.

In (6) use same valences as in (2), and note the formation of ortho-acids.

In (7) that the ortho-acids from non-metals and metals containing more than two (OH) groups split off H_2O to form meta-acids (exceptions, H_3BO_3, H_4SiO_4); generally sufficient H_2O is split off to reduce the H to one or two atoms, the intermediate meta-acids being unstable (exceptions, H_3PO_4, H_3AsO_4).
Of the more important acids, H_3PO_2 hypophosphorous acid, H_3PO_3 phosphorous acid, and $H_2S_2O_3$ thiosulphuric acid, are constituted differently from the other acids.

In (8) by writing each (OH) of the base and each H of the acid separately and opposite to each other, note that in the formation of salts the OH from the base and the H from the acid combine to form H_2O, which is a second product of the reaction; a glance will tell if only a normal salt is possible, or basic or acid salts in addition to the normal salt; thus, **a** with **e**; **b** with **f**; and **c** with **g** will give *normal* salts only.
a with **f**, **g** and **h**; **b** with **g** and **h**; and **c** with **h** will give *acid* as well as *normal* salts.
b, **c** and **d** with **e**; **c** and **d** with **f**; **d** with **g** and **h** will give *basic* as well as *normal* salts.

In addition to the naming of Compound Molecules, as indicated in the valence tables, provision must be made to distinguish between several salts of the same base and acid. If but one acid or basic salt is known in addition to the normal salt, three methods are in use:

1. The word *acid* or *basic* is used to qualify the name of the normal salt.
2. The prefix *Bi* is attached to the acid part of the name of the normal salt to indicate the acid salt, while the prefix *Sub* is used in the same way to indicate the basic salt.
3. The use of numeral prefixes as explained below.

When several acid or basic salts are possible, the best method of distinguishing between them is to apply numeral prefixes to that part of the name of the normal salt which is present in varying quantities; thus in the case of acid salts the numeral prefix used corresponds to the number of atoms of metal present in the salt; in the case of basic salts the numeral prefix indicates the number of acid radicals in the formula.

This same method of using numeral prefixes is used at times to name Binary Molecules, and is useful in naming compounds in which we meet with exceptional valences, or in which confusion has arisen through the improper use of the suffixes *ous* and *ic;* but to apply it indiscriminately to all Binary Molecules seriously interferes with the student's perception of the system of chemical nomenclature, based upon valence, as shown in the charts.

Chemical Changes or Reactions

may take place between two substances without physical aid, but by far the largest number take place in presence of water (or some other solvent), or the reaction must be started by heating to a suitable temperature; in most cases the solvent or heat weakens the force of cohesion in the original molecules and enables rearrangement of the atoms; in other cases the water dissolves the product of the reaction and prevents the product from coating or incrusting the reacting substances which would stop the action.

Water as a rule acts only as a solvent, but in some cases it enters into the reaction to form bases or acids and basic or acid salts.

HEAT will also bring about certain changes, especially, if by rearrangement a product can be formed which is gaseous or volatile.

ELECTRICITY can cause either combination of elements or decomposition of compound molecules, the latter property being utilized in electrolysis of solutions or of fused substances.

LIGHT may also bring about chemical combinations, especially of gases, or decompositions as seen in the changes of the salts of mercury and silver, the latter in photographic exposure being most important.

Most Chemical Reactions are explainable upon **the position of the elements in the Electro-Chemical Series,** the rule being that opposites attract, and that the greater the distance between two elements in the series the stronger will be the compound with some other element or groups of elements; in other words, a stronger electro-negative element will displace a weaker electro-negative element, or a stronger electro-positive element will displace a weaker electro-positive element from combination. As chemical reactions always represent molecular changes, the student's attention is called to the fact that an element entering or issuing from a reaction does so in molecular form: for number of atoms in elemental molecules see page 1.

A large number of reactions are the result of double decomposition, an exchange of either the electro-positive or the electro negative parts of two molecules.

Exceptions to the above general rule are founded upon

1. **The formation of precipitates or insoluble substances.** This law is expressed as follows: Whenever, on mixing two substances in solution, a molecule can be formed by a rearrangement of the atoms which is insoluble in the menstruum employed, such a molecule will be formed, and will appear as a precipitate.

   $$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl; \qquad 2H_2S + 2I_2 = 4HI + S_2.$$

   Both of these reactions are in opposition to the positions in the Electro-Chemical Series, but easily explainable by the insolubility of $BaSO_4$ and of S.

2. **The formation of gaseous or volatile substances,** embodied in the following law: Whenever, by the action of substances upon each other, any molecule, volatile at the temperature of the experiment, can be formed by a rearrangement of the atoms, such a rearrangement will take place and such a molecule will be evolved as a gas or vapor.

   $$2H_3N + 3Br_2 = 6HBr + N_2; \qquad 2KClO_3 + 2I_2 = 2KIO_3 + 2ICl;$$
   $$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4; \qquad FeS + H_2SO_4 = FeSO_4 + H_2S.$$

   Of these reactions the first is in opposition to the Electro-Chemical Series and explained by the liberation of N; the second is only an apparent exception, as the Cl is combined with the O and there is a greater affinity between the I and O; the third and fourth agree with the Electro-Chemical Series.

3. **Some oxidation and reduction changes** between Compound Molecules,

Classification of Reactions.

A. Direct Union of

1. Elements to form Binary Molecules:

$C_2 + O_2 = 2CO$; $C_2 + 2O_2 = 2CO_2$; $Hg + I_2 = HgI_2$;
$Au_2 + 3Cl_2 = 2AuCl_3$; $I_2 + Cl_2 = 2ICl$.

2. Base-forming Oxides with H_2O to form Bases:

$CaO + H_2O = Ca(OH)_2$; $MgO + H_2O = Mg(OH)_2$.

3. Base-forming Oxides with Acid-forming Oxides to form Salts:

$CaO + CO_2 = CaCO_3$; $2MgO + P_2O_5 = Mg_2P_2O_7$.

4. Acid-forming Oxides with H_2O to form Acids:

$SO_2 + H_2O = H_2SO_3$; $P_2O_5 + 3H_2O = 2H_3PO_4$; $Cl_2O + H_2O = 2HClO$.

5. Two Compound Molecules to form Double Salts, in which the two positive atoms preserve their character:

$Al_2(SO_4)_3 + K_2SO_4 = Al_2K_2(SO_4)_4$; $Fe_2(SO_4)_3 + (NH_4)_2SO_4 = Fe_2(NH_4)_2(SO_4)_4$.

6. Two Compound Molecules to form Double Salts, in which one of the positive atoms acts as part of an acid:

$HgI_2 + 2KI = K_2HgI_4$; $4KCN + Fe(CN)_2 = K_4Fe(CN)_6$; $6KCN + Fe_2(CN)_6 = K_6Fe_2(CN)_{12}$;
$HgS + Na_2S = Na_2HgS_2$; $PtS_2 + 2Na_2S = Na_4PtS_4$; $As_2S_3 + 3Na_2S = 2Na_3AsS_3$.

B. Double Decomposition between

1. Base-forming Oxides with Acids to form Salts:

$CaO + 2HCl = CaCl_2 + H_2O$; $MgO + 2HNO_3 = Mg(NO_3)_2$.

2. Acid-forming Oxides with Bases to form Salts:

$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$; $2KOH + SO_2 = K_2SO_3 + H_2O$.

3. Acids and Bases to form Salts:

$Fe_2(OH)_6 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O$; $Al_2(OH)_6 + 6HCl = Al_2Cl_6 + 6H_2O$.

4. Basic Salts with Acids to form Normal Salts:

$BiONO_3 + 2HNO_3 = Bi(NO_3)_3 + H_2O$.

5. Acid Salts with Bases to form Normal Salts:

$KHSO_4 + KOH = K_2SO_4 + H_2O$.

6. Bases (or H_2O) upon Normal Salts to form Basic Salts:
$BiCl_3 + 2NH_4OH = BiOCl + 2NH_4Cl$; $BiCl_3 + H_2O = BiOCl + 2HCl$.

7. Acids (or H_2O) upon Normal Salts to form Acid Salts:
$K_2CO_3 + H_2O + CO_2 = 2KHCO_3$; $Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$;
$Na_4As_2O_7 + H_2O = 2Na_2HPO_4$.

8. Compound Molecules upon each other; *without secondary reaction:*
$FeS + H_2SO_4 = FeSO_4 + H_2S$; $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$;
$NaCl + H_2SO_4 = NaHSO_4 + HCl$;
$NaHSO_4 + NaCl = Na_2SO_4 + HCl$; $AgNO_3 + HCl = AgCl + HNO_3$.
$3AgNO_3 + H_3Sb = Ag_3Sb + 3HNO_3$.
$CdSO_4 + H_2S = CdS + H_2SO_4$; $BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$.
$Fe_2Cl_6 + 6NH_4OH = Fe_2(OH)_6 + 6NH_4Cl$; $ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$.
$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$; $Al_2(OH)_6 + 6NaOH = Na_6Al_2O_6 + 6H_2O$.

9. COMPOUND MOLECULES upon each other ; *with secondary reaction, due to the instability of the expected molecule :*

$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$;
$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2$;
$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl$;
$2AgNO_3 + 2KOH = Ag_2O + H_2O + 2KNO_3$.
$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Al_2(OH)_6 + 3Na_2SO_4 + 3CO_2$;
$Cr_2Cl_6 + 3(NH_4)_2S + 3H_2O = Cr_2(OH)_6 + 6NH_4Cl + 3H_2S$;
$Na_2HgS_2 + 2HCl = HgS + 2NaCl + H_2S$;
$2Na_3AsS_3 + 6HCl = As_2S_3 + 6NaCl + 3H_2S$.

C. Action of Elements upon Compound Molecules with Separation of other Elements.

$Zn + H_2SO_4 = ZnSO_4 + H_2$;
$Zn + 2KOH = K_2ZnO_2 + H_2$;
$2HgCl_2 + Cu_2 = 2CuCl_2 + 2Hg$;
$4SbCl_3 + 3Sn_2 = 6SnCl_2 + 2Sb_2$;
$2KI + Cl_2 = 2KCl + I_2$;
$2KI + Br_2 = 2KBr + I_2$;
$2ZnO + C_2 = 2CO + 2Zn$;

$Fe_2 + 4HCl = 2FeCl_2 + 2H_2$;
$Al_2 + 6NaOH = Na_6Al_2O_6 + 3H_2$;
$2CuCl_2 + Fe_2 = 2FeCl_2 + Cu_2$;
$4SbCl_3 + 3Fe_2 = 6FeCl_2 + 2Sb_2$.
$2KBr + Cl_2 = 2KCl + Br_2$;
$2KClO_3 + I_2 = 2KIO_3 + Cl_2$.
$2As_2O_3 + 3C_2 = 6CO + As_4$.

D. Oxidation and Reduction.

In the narrowest sense, the former means combination with O; the latter the separation of an element, under favorable conditions, through the influence of a stronger element. In the broadest sense, oxidation implies an increase, reduction a decrease in valence.

An oxidizing agent in doing work suffers a decrease, a reducing agent an increase in valence ; oxidation and reduction are, therefore, compensatory chemical changes, and may take place, depending upon the nature of the reagent, in acid, alkaline or neutral solutions.

Oxidizing and reducing agents may act directly or indirectly ; in the latter case water, essential to the reaction, is decomposed and the O or H causes oxidation or reduction.

REDUCING AGENTS : H (nascent or atomic, prepared in the presence of the substance to be reduced, is most active, and active at low temperatures ; molecular H is only active if assisted by high temperatures), metals, C, S, HI, HBr, HCl, H_2O_2, H_2S, H_2SO_2, SO_2, $Na_2S_2O_3$, $SnCl_2$, As_2O_3, HNO_2, Ferrous Salts, etc., etc.

OXIDIZING AGENTS : O, Cl, Br, I, H_2O_2, As_2O_3, As_2O_5, HClO, $HClO_3$, $HBrO_3$, HIO_3, HNO_2, HNO_3, H_2SO_4, $H_2S_2O_8$, CrO_3, MnO_2, $K_2Cr_2O_7$, $K_2Mn_2O_8$, K_2MnO_4, Ferric, Cupric, Mercuric, Silver and Gold Salts, etc., etc.

As will be noticed, oxidizing and reducing agents may be either Elemental or Compound Molecules ; in the case of salts the action may be due either to the Base-forming or the Acid-forming Element.

Oxidation and Reduction Reactions may be classified because of the action of :

1. HYDROGEN COMPOUNDS of the more active NON-METALS upon ACID-FORMING OXIDES or ACIDS ; positive and negative (or base-forming and acid-forming) valences of the same element, under proper conditions of solution and temperature, are antagonistic, and result in the liberation of the element or the formation of a more stable compound of intermediate valence.

$NaCl + NaClO + 2HCl = 2NaCl + H_2O + Cl_2$;
$4HCl + 2KClO_3 = 2KCl + 2H_2O + Cl_2O_4 + Cl_2$;
$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$;
$NaI + NaIO + H_2SO_4 = Na_2SO_4 + H_2O + I_2$;
$5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3Br_2$.

$4H_2S + 2SO_2 = 4H_2O + 3S_2$;
$4H_2S + 2H_2SO_3 = 6H_2O + 3S_2$;
$2H_2S + 2H_2SO_4$ (conc.) $= 4H_2O + 2SO_2 + S_2$;
$PbS + PbSO_4 = Pb_2 + 2SO_2$
NH_4NO_3 or $(NH_3 + HNO_3) = 2H_2O + N_2O$;
NH_4NO_2 or $(NH_3 + HNO_2) = 2H_2O + N_2$.
$3MnO + Mn_2O_7 = 5MnO_2$;
$3MnSO_4 + K_2Mn_2O_8 + 2H_2O = K_2SO_4 + 2H_2SO_4 + 5MnO_2$;
$2KI + NaClO + 2HCl = 2KCl + NaCl + H_2O + I_2$;
$2KI + 2HNO_2 + H_2SO_4 = K_2SO_4 + 2H_2O + N_2O_2 + I_2$;
$6KI + K_2Cr_2O_7 + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$;
$10KI + K_2Mn_2O_8 + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$;
$3HCl + HNO_3 = 2H_2O + NOCl + Cl_2$ (Aqua Regiæ);
$5H_2S + 8KIO_3 = 4K_2SO_4 + H_2SO_4 + 4H_2O + 4I_2$;
$2H_2S + 2HClO = 2HCl + 2H_2O + S_2$;
$6H_2S + 4HNO_3 = 8H_2O + 2N_2O_2 + 3S_2$;
$6H_2S + 4H_2CrO_4 + 12HCl = 2Cr_2Cl_6 + 16H_2O + 3S_2$;
$10H_2S + 2K_2Mn_2O_8 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5S_2$.
$H_3As + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 3Ag_2$.

2. ELEMENTS upon COMPOUND MOLECULES.

$2I_2 + 2H_2S = 4HI + S_2$;
$I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4$;
$I_2 + H_2O + Na_2SO_3 = 2HI + Na_2SO_4$;
$2I_2 + 2H_2O + As_2O_3 = 4HI + As_2O_5$;
$2I_2 + 2H_2O + Sb_2O_3 = 4HI + Sb_2O_5$;
$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$;
$Br_2 + 2KOH = KBr + KBrO + H_2O$;
$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O$;
$4Br_2 + 4H_2O + Ca(H_2PO_2)_2 = CaH_4(PO_4)_2 + 8HBr$;
$3Cl_2 + 6FeSO_4 = 2Fe_2(SO_4)_3 + Fe_2Cl_6$.
$2Cl_2 + 2HgS = 2HgCl_2 + S_2$.
$Zn + H_2SO_4 + Fe_2Cl_6 = 2FeCl_2 + ZnSO_4 + 2HCl$.
$3Zn + 7H_2SO_4 + K_2Cr_2O_7 = Cr_2(SO_4)_3 + K_2SO_4 + 3ZnSO_4 + 7H_2O$.
$5Zn + 8H_2SO_4 + K_2Mn_2O_8 = 2MnSO_4 + K_2SO_4 + 5ZnSO_4 + 8H_2O$.
$6Zn + 6H_2SO_4 + As_2O_3 = 2H_3As + 6ZnSO_4 + 3H_2O$.
$6Zn + 12KOH + As_2O_3 = 2H_3As + 6K_2ZnO_2 + 3H_2O$.
$Pb_2 + 2KNO_3 = 2PbO + 2KNO_2$.
$8Zn + 9H_2SO_4 + 2HNO_3 = (NH_4)_2SO_4 + 8ZnSO_4 + 6H_2O$.
$4Zn + 8KOH + HNO_3 = NH_3 + 4K_2ZnO_2 + 3H_2O$.
$2Zn + 2H_2SO_4 + H_3PO_2 = H_3P + 2ZnSO_4 + 2H_2O$.
$2S_2 + 3Ca(OH)_2 = 2CaS + CaS_2O_3 + 3H_2O$.
$2S_2 + 3K_2CO_3 = 2K_2S + K_2S_2O_3 + 3CO_2$.
$S_2 + 2Na_2SO_3 = 2Na_2S_2O_3$.
$5S_2 + 12KNO_3 + 4K_2CO_3 = 10K_2SO_4 + 4CO_2 + 6N_2$.
$S_2 + 4H_2SO_4 = 4H_2O + 6SO_2$.
$Cu_2 + 4H_2SO_4 = 2CuSO_4 + 4H_2O + 2SO_2$.
$C_2 + 2ZnO = 2Zn + 2CO$.
$C_2 + 2CaCO_3 = 2CaO + 4CO$.
$C_2 + 4H_2SO_4 = 4H_2O + 2CO_2 + 4SO_2$.
$2C_2 + Na_2SO_4 = Na_2S + 4CO$.
$3C_2 + 2KBrO_3 = 2KBr + 6CO$.
$5C_2 + 8KNO_3 = 4K_2CO_3 + 6CO_2 + 4N_2$.

3. Compound Molecules (not included in 1) upon each other.

To understand **Oxidation** and **Reduction Reactions**, the student should note the changes in valence and balance the equation upon these, remembering that the decrease in valence of the oxidizing agent must be exactly compensated for by an increase in valence of the reducing agent or substance which is oxidized. To illustrate, **Nitric Acid** as an oxidizing agent generally decomposes as follows: $2HNO_3 = H_2O + N_2O_2 + O_3$. The two atoms of N before doing oxidizing work have a combined valence of *ten*, after doing oxidizing work they have a combined valence of *four:* the decrease is *six*, the valence of the three available O atoms.

Applied to the oxidation of $FeSO_4$, note that two atoms of Fe in $FeSO_4$, with a combined valence of *four*, must be used to obtain the Fe(ic) (Fe_2) group with a valence of *six:* an increase of *two*, corresponding to one atom of O. Therefore in the oxidation of $FeSO_4$ by HNO_3 two molecules of HNO_3, suffering a *decrease of six* in the valence of the N atoms, will oxidize six molecules of $FeSO_4$, requiring an *increase of six* in the valence of the Fe atoms. The O from the oxidizing agent in reactions of this kind in which base-forming or salt-forming valences result performs the duty of satisfying the increased valence forming basic or oxy-salts; but in the presence of free acid the H of this and the O from the oxidizing agent combine to form H_2O, and the acid radical of the acid then satisfies the increased valence of the metal forming a normal salt: $2FeSO_4 + O = Fe_2O(SO_4)_2$; $Fe_2O(SO_4)_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O$.

Concentrated Sulphuric Acid, as an oxidizing agent: $H_2SO_4 = H_2O + SO_2 + O$.

Potassium Dichromate, in solution, as a rule, oxidizes only in presence of acids: $K_2Cr_2O_7 = K_2O + Cr_2O_3 + O_3$.

Potassium Permanganate, in acid solution: $K_2Mn_2O_8 = K_2O + 2MnO + O_5$; in alkaline or neutral solution: $K_2Mn_2O_8 = K_2O + 2MnO_2 + O_3$.

$H_2O_2 + Mn(OH)_2 = MnO_2 + 2H_2O$.
$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2$.
$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.
$5Ca(H_2PO_2)_2 + 2K_2Mn_2O_8 + 6H_2SO_4 = 5Ca(H_2PO_3)_2 + 2K_2SO_4 + 4MnSO_4 + 6H_2O$.
$3Ca(H_2PO_3)_2 + 2K_2Mn_2O_8 + 2H_2SO_4 = 3CaH_4(PO_4)_2 + 2K_2SO_4 + 4MnO_2 + 2H_2O$.
$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$.
$3Pb_3O_4 + 2MnO_2 + 18HNO_3 = 9Pb(NO_3)_2 + 8H_2O + H_2Mn_2O_8$.
$5H_2C_2O_4 + K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$.
$PtCl_4 + SnCl_2 = PtCl_2 + SnCl_4$.
$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$.
$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$.
$Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$.
$2As_2O_5 + 10SnCl_2 + 20HCl = 10SnCl_4 + 10H_2O + As_4$.
$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + N_2O_2$.
$2FeSO_4 + 2CuSO_4 = Fe_2(SO_4)_3 + Cu_2SO_4$.
$6FeSO_4 + 2AuCl_3 = 2Fe_2(SO_4)_3 + Fe_2Cl_6 + Au_2$.
$2FeSO_4 + HClO + H_2SO_4 = Fe_2(SO_4)_3 + H_2O + HCl$.
$6Fe(OH)_2 + KClO_3 + 3H_2O = 3Fe_2(OH)_6 + KCl$.
$Mn(OH)_2 + NaClO = MnO_2 + H_2O + NaCl$.
$Cr_2(OH)_6 + 3NaClO + 4NaOH = 2Na_2CrO_4 + 3NaCl + 5H_2O$.
$2Na_2S_2O_3 + NaClO + H_2O = 2NaOH + Na_2S_4O_6 + NaCl$.
$Fe_2Cl_6 + 6KI = 6KCl + 2FeI_2 + I_2$.
$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$.
$4HgCl_2 + H_3PO_2 + 2H_2O = H_3PO_4 + 2Hg_2Cl_2 + 4\ HCl$.
$5SO_2 + 2KIO_3 + 4H_2O = K_2SO_4 + 4H_2SO_4 + I_2$.
$4PbO + 2PbS = 3Pb_2 + 2SO_2$.
$6PbS + 16HNO_3 = 6Pb(NO_3)_2 + 2N_2O_2 + 8H_2O + 3S_2$.

4. Two Oxidizing or Two Reducing Agents upon each other.

$H_2O_2 + NaClO = H_2O + NaCl + O_2$.
$H_2O_2 + K_6Fe_2(CN)_{12} + 2KOH = 2K_4Fe(CN)_6 + 2H_2O + O_2$.
$2H_2O_2 + K_2Cr_2O_7 = K_2Cr_2O_7 + 2H_2O + O_2$.
$3H_2O_2 + K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$.
$5H_2O_2 + K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$.
$H_2O_2 + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$.
$H_2O_2 + Ag_2O = Ag_2 + H_2O + O_2$.
$4H_2S + 2SO_2 = 4H_2O + 3S_2$.
$2H_3PO_2 + 2H_2SO_3 = 2H_3PO_4 + 2H_2O + S_2$.
$2As_2O_3 + 6H_3PO_2 = 6H_3PO_3 + As_4$.
$2As_2O_3 + 6SnCl_2 + 12HCl = 6SnCl_4 + 6H_2O + As_4$.

5. CERTAIN SUBSTANCES which THEMSELVES UNDERGO NO CHANGE (CATALYSIS)

$MnO_2 + 2KClO_3 = MnO_2 + 2KCl + 3O_2$.
$MnO_2 + 2H_2O_2 = MnO_2 + 2H_2O + O_2$.
$Fe_2Cl_6 + 2H_2O_2 = Fe_2Cl_6 + 2H_2O + O_2$.
$Co_2O_3 + 2NaClO = Co_2O_3 + 2NaCl + O_2$.
$2K_2Cr_2O_7 + 2H_2O_2 = 2K_2Cr_2O_8 + 2H_2O$;
$2K_2Cr_2O_8 = 2K_2Cr_2O_7 + O_2$.

E. Decomposition by Heat.

Some of these changes take place at low temperatures and in presence of water; others require a red heat. Metals or Metallic Groups, with the exception of Mercury, Ammonium and some Arsenous Compounds, are not volatile; therefore, the Metals are found either free or in some form of combination in the residue after heating.
The Non-metals and Acid-groups are, as a rule, decomposed or volatile, and these are more or less changed by heat.

$PtCl_4 = PtCl_2 + Cl_2$; $2PtCl_2 = Pt_2 + 2Cl_2$;
$2AuCl_3 = Au_2 + 3Cl_2$; $3NaClO = 2NaCl + NaClO_3$;
$6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2$; $2KClO_3 = KCl + KClO_4 + O_2$;
$KClO_4 = KCl + 2O_2$.
$2Ag_2O = 2Ag_2 + O_2$; $2HgO = 2Hg + O_2$;
$2BaO_2 = 2BaO + O_2$; $3MnO_2 = Mn_3O_4 + O_2$.
$NH_4OH = NH_3 + H_2O$; $Mg(OH)_2 = MgO + H_2O$;
$Fe_2(OH)_6 = Fe_2O_3 + 3H_2O$.
$2FeS_2 = 2FeS + S_2$; $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S + 2S_2$;
$CuS_2O_3 + H_2O = CuS + H_2SO_4$; $2NaHSO_4 = Na_2S_2O_7 + H_2O$.
$NH_4NO_2 = 2H_2O + N_2$; $NH_4NO_3 = 2H_2O + N_2O$;
$2KNO_3 = 2KNO_2 + O_2$; $2Ca(NO_3)_2 = 2CaO + 2N_2O_4 + O_2$;
$Hg_2(NO_3)_2 = 2HgO + N_2O_4$; $2Hg(NO_3)_2 = 2HgO + 2N_2O_4 + O_2$;
$4Bi(OH)_2NO_3 = 2Bi_2O_3 + 4H_2O + 2N_2O_4 + O_2$.
$NaH_2PO_4 = NaPO_8 + H_2O$; $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$;
$2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$;
$20NaH_2PO_2 = 4NaPO_3 + 4Na_4P_2O_7 + 4H_3P + 14H_2 + P_4$.
$H_2CO_3 = H_2O + CO_2$; $2KHCO_3 = K_2CO_3 + H_2O + CO_2$;
$CaCO_3 = CaO + CO_2$; $2K_2C_4H_4O_6 = 2K_2CO_3 + 4H_2O + 2CO + 2C_2$;
$2NaC_2H_3O_2 = Na_2CO_3 + C_3H_6O$.
$H_2SiO_3 = H_2O + SiO_2$.

Physical Properties Utilized in Chemical Analysis.

ANALYTICAL CHEMISTRY is that branch of the science which determines the presence or absence of the elements in their several forms of combination; this is possible by studying the material under examination, in its behavior towards other chemical substances, called reagents, which bring about certain chemical changes, the new products of which possess easily observable physical properties.

I. **Depending upon Solubility:**

- A. FORMATION OF INSOLUBLE COMPOUNDS OR PRECIPITATES;
- B. FORMATION OF SOLUBLE COMPOUNDS FROM PRECIPITATES.

II. **Depending upon Change of Color:**

- A. BEHAVIOR TO TEST PAPERS;
- B. BEHAVIOR IN BUNSEN FLAME (FLAME TESTS);
- C. BEHAVIOR IN FUSED BORAX (BORAX BEADS);
- D. PRODUCTION OF COLORED SOLUTIONS;
- E. PRODUCTION OF COLORED RESIDUES ON PORCELAIN;
- F. PRODUCTION OF COLORED INCRUSTATIONS ON CHARCOAL;
- G. PRODUCTION OF COLORED RESIDUES ON CHARCOAL, AFTER TREATMENT WITH $Co(NO_3)_2$.

III. **Depending upon the Formation of a Gaseous or Volatile Substance:**

- A. THE VOLATILE PRODUCT IS SOUGHT FOR;
- B. THE NON-VOLATILE PRODUCT IS SOUGHT FOR.

Explanatory Notes on the above Classification of Physical Properties.

IA. As by far the largest number of changes utilized in Analytical Chemistry depend upon solubility, it is of the greatest importance to know, or to be able to refer to, the solubility of the compound forming the basis of the test. For this reason a comprehensive Table of the Solubilities of Compound Molecules is furnished, embodying in case of instability of the molecule, the product resulting from its decomposition.

IB. The solubility of water-insoluble compounds in the stronger mineral acids depends generally upon double decomposition, and results in the formation of a salt of the acid employed with the liberation of the H compound of the negative constituent, which is usually an acid, but will be hydrogen oxide, hydrogen sulphide, etc., if the insoluble compound be an oxide, sulphide, etc. In testing this solubility the acid selected should not form an insoluble compound with the metallic or basic constituent. In some cases, as in the solubility of phosphates in acids, the latter abstract part of the base to form a salt, leaving the balance with all of the acid of the insoluble compound to form a soluble acid salt. In other cases, as in the insoluble carbonates, cyanides, borates, iodides, phosphates, sulphides, sulphites, thiosulphates, etc., an excess of the corresponding acid or of the salt producing the insoluble compound may cause solution by the formation of either acid salts or of double salts.

Key to the Table of Solubility and Stability of Chemical Compounds.

1. Soluble in water.
2. Soluble in water, but with a tendency to form basic salts, insoluble in water, soluble in acids.
3. Decomposed by water into basic or oxy-salts, insoluble in water, soluble in acids.
4. Slightly soluble in water, readily soluble in acids (may separate organic acid, if this be not very soluble).
5. Slightly soluble in water and in acids.
6. Insoluble in water, readily soluble in acids.
7. Insoluble in water, slightly soluble in acids.
8. Insoluble in water, decomposed by acids with separation of the acid from the insoluble compound.
9. Insoluble in water and in acids.
10. Forms Hydrate, insoluble in water, soluble in acids.
11. Forms Metallic oxide, insoluble in water, soluble in acids.
12. Forms Non-metallic oxide, insoluble or slightly soluble in water, soluble in alkalies.
13. Forms Sulphide, insoluble in water, sparingly soluble in acids.
14. Insoluble in water, decomposed by acids; slowly decomposes into Sulphide, but very rapidly on heating.
15. Decomposed, one part oxidized at expense of the other part which is reduced.
16. Decomposed, valence reduced.
17. Valence reduced in neutral or acid solution.
18. Valence reduced in alkaline solution.
19. Metal separates in neutral or acid solution.
20. Valence reduced ; with excess of reducing agent, metal separates in neutral or acid solution.
21. Valence increased; resulting oxide soluble in acid.
22. Valence increased; resulting oxide insoluble in water and dilute acid; concentrated HCl liberates Cl and again reduces valence.
23. Valence increased in alkaline solution; resulting oxide decomposed by concentrated HCl with liberation of Cl.
24. Valence increased in alkaline solution; resulting oxide is acid-forming, hence, soluble in alkalies.
25. Slightly soluble in water, soluble in acids; upon long keeping, or upon boiling, metal separates.
26. Insoluble in water, soluble in acids ; in presence of alkalies, valence is reduced.
27. Slightly soluble in water, soluble in acids; in presence of alkalies, metal separates.
28. Insoluble in water, soluble in acids; in presence of alkalies, metal separates.
29. Slightly soluble in water, soluble in acids; in presence of alkalies, valence is increased; resulting oxide decomposed by concentrated HCl with liberation of Cl.

Table of Solubility and Stability of Chemical Compounds.

	Al_2 VI	Ag I	Au III	Ba II	Bi III	Ca II	Cd II	Ce_2 VI	Co II	Cr_2 VI	Cu II	Fe II	Fe_2 VI	H I	Hg II	Hg_2 II	K I	Li I	Mg II	Mn II	Na I	NH_4 I	Ni II	Pb II	Pt IV	Sb III	Sn II	Sn IV	Sr II	Zn II
Acetate	2	4	1	1	1	1	1	1	1	2	1	1	2	1	1	4	1	1	1	1	1	1	1	1		1	1	1	1	1
Arsenate	6	6		6	6	6		6	6	6	6	6	6	1	6	6	1	6	6	6	1	1	6	6	6	7	19	6	6	6
Arsenite		28	19	4		6			6		26	6	18	12	26	6	1		4	6	1	1	6	6	17	6	19	6	6	6
Benzoate	1	4	4	4	4	1	4	1	1	4	4	1	4	5	4	4	1	1	1	1	1	1	1	4	4	1	4	4	4	1
Borate	4	4		4	6	4	4		4	6	6	6	6	1	6	6	1	1	4	4	1	1	6	4			6		4	6
Bromate	1	4		1	6	1	1	1	1	1	1	1	1	1	1	4	1	1	1	1	1	1	1	1	1		6	1	1	1
Bromide	1	9	1	1	3	1	1	1	1	1	1	1	1	1	5	7	1	1	1	1	1	1	1	5	1	3	2	1	1	1
Carbonate	10	6		6	6	6	6	6	6	6	6	6	10	12	6	11	1	4	6	6	1	1	6	6	1	10	10	10	6	6
Chlorate	1	1		1	1	1	1		1	1	1	21	1	1	1	1	1	1	1	1	1	1	1	1			21		1	1
Chloride	1	9	1	1	3	1	1	1	1	1	1	1	1	1	1	9	1	1	1	1	1	1	1	5	1	3	2	2	1	1
Chromate	6	6		6	6	1	4	6	4	6	4	21	6	12	4	6	1	1	1	1	1	1	4	7	6	6	21		1	1
Citrate	1	6		4	6	1	4	6	1	1	1	1	1	1	4	6	1	1	1	6	1	1	1	6		1			4	4
Cyanide		7	1	1		1	6	6	7	6	6	7	1	1	1	15	1		1	6	1	1	7	4	7			10	1	6
Ferricyanide		9		1	7	1	6	1	9	24	9	9	1	1	1		1		1	9	1	1	9	29			6		1	6
Ferrocyanide	7	7		4	7	1	6	6	9		9	9	9	1			1		1	6	1	1	9	9			9		1	7
Fluoride	1	1		7	1	7	4	6	4	1	4	4	1	1	4	1	1	1	7	6	1	1	4	4	1	1	1	1	7	4
Formate	2	25	19	1	1	1	1	4	4	1	1	1	2	1	17	25	1	1	1	1	1	1	4	4	19				1	1
Gallate	4	19	19	4	4	4	1		4		17	4	4	5	4	4	1	1	1	1	1	1	1	4	17	4	4		4	4
Hydrate	6	11	11	1	6	4	6	6	6	6	6	6	6	1	11	11	1	1	6	6	1	1	6	6		6	6	6	4	6
Hypochlorite	1	15		1		1		23	23	24	1	21		1		21	1			22	1	16	23	23		24			1	1
Hypophosphite	1	19	19	1		1	1		1	1	19	1	6	1	20	19	1		1	1	1	1	1	1	19				1	1
Iodide	1	9	1	1	3	1	1	1	1	1	17	1	17	1	7	7	1	1	1	1	1	1	1	5	1	3	2	2	1	1
Lactate	4	1	19	1	4	1	1		1	1	1	1	1	1	1	4	1	1	1	1	1	1	4	1		4	6	1	1	1
Malate	1	4		4		1					1	1	1	1	4	6	1	1	1	1	1	1		4			1	1	1	1
Nitrate	1	1	1	1	3	1	1	1	1	1	1	21	1	1	3	3	1	1	1	1	1	1	1	1	1		10	10	1	1
Nitrite		4	19	1		1			21		1	21		12	1	19	1		1	1	1	1	1	1					1	
Oleate	8	8		8	8	8	8	8	8	8	8		8	9	8		1		8	8	1	1	8	8			8		8	8
Oxalate	4	6	19	4	6	6	6	7	6	1	6	7	4	1	7	7	1	1	4	4	1	1	6	6	17	4	6		6	6
Oxide	6	6	6	1	6	4	6	7	6	7	6	7	7	1	6	6	1	1	6	6	1	16	6	6		7	6	7	4	6
Permanganate		4		1		1					1	21	1	1			1	1	1	22	1	1		4		24			1	1
Metaphosphate	6	6		6	6	6	6		6	6	6	1	6	1	4	4	1		6	6	1		6	6					6	6
Orthophosphate	6	6	6	6	6	6	6	6	6	6	6	6	6	1	6	6	1	4	6	6	1	1	6	6		4		7	6	6
Pyrophosphate	6	6		4	6	4	6	6	6	6	6	6	6	1	6	6	1		4	6	1	1	6	6		6			4	6
Salicylate		4		1	4	1	1					1	1	5		4	1	1	1		1	1		4						1
Silicate	7			7		7		6	6	6	6	6	6	7			1	6	7	6	1		6	6					6	6
Stearate	8	8		8	8	8	8	8	8	8	8		8	9	8		1		8	8	1	1	8	8			8		8	8
Succinate	4	4		4	4	1	6	6	4	6	4	1	2	1	4	6	1	1	1	1	1	1	1	4		1	6	6	4	4
Sulphate	1	4	1	9	2	5	1	1	1	1	1	1	1	1	3	3	1	1	1	1	1	1	1	7	1	6	2	10	9	1
Sulphide	10	7	7	1	6	4	6	10	7	10	6	6	17	1	7	15	1	1	1	6	1	1	7	6	7	6	6	6	1	6
Sulphite	4	14	19	6	6	1	4	1	4	4	17	4	17	12	17	6	1	1	4	4	1	1	6	6	17	6	21		6	4
Sulphocarbolate				1		1					1	1		1			1		1		1	1		1						1
Sulphocyanate	1	7	1	1	6	1	1	1	1	1	17	1	1	1	5	6	1	1	1	1	1	1	1	4	1		1	1		1
Tannate		19	19	4		4	6				6		6	1	28	28	1				1	1		6	17	4	6	6		6
Tartrate	1	27	19	4	6	4	4	4	1	1	6	1	1	1	6	4	1	1	4	4	1	1	6	6		1			4	4
Thiosulphate	10	13	1	4		1	1		13	10	14		17	12	14	13	1		1	1	1	1	1	14					1	1
Valerianate	6	4		1	6	1	1		1		1	4	6	1	4		1	1	1	1	1	1	1	1			1		1	1

IIA. TEST PAPERS are used for one of three purposes:

1. To add a definite quantity of reagent in a test, thus avoiding an excess which might interfere with the success of the test: Nitro-prusside of Sodium and Indigo Test Papers; in the former the color of the reagent added in excess simulates the rose-color produced in the test for H_2SO_3; in the latter an excess of Indigo solution would not be decolorized by the quantity of the acid to be tested for.
2. To indicate when a sufficient quantity of a reagent has been added to neutralize a previously added reagent, as in the case of Red and Blue Litmus Papers in neutralizing acids and alkalies.
3. To indicate the presence or absence of substances to be tested for, as in the case of:
   - *a.* Blue Litmus Paper in the recognition of acids or substances having an acid reaction.
   - *b.* Red Litmus Paper for substances having an alkaline reaction, as in tests for NH_4 and for some salts.
   - *c.* Turmeric Paper for **H_3BO_3**.
   - *d.* Starch Paper for **free I**.
   - *e.* Starch and KI Paper for **Cl**, **Br**, N_2O_3, **H_2CrO_4**, **$H_2Mn_2O_8$**, etc.
   - *f.* Starch and KIO_3 Paper for **H_2S** and **SO_2**.
   - *g.* Lead Acetate ($Pb\bar{A}_2$) Paper for **H_2S**.
   - *h.* Nitro-prusside Paper for **H_2S** and **H_2SO_3**.
   - *i.* Indigo Test Paper for **Cl**, **HClO**, **$HClO_3$**, **Br**, **H_2S**, **H_2SO_2**, **HNO_2**, **HNO_3**, **H_3PO_2**, **$H_6Fe_2(CN)_{12}$**, **H_2CrO_4**, **$H_2Mn_2O_8$**.

B. PRODUCTION OF COLORED SOLUTIONS. The following are used as tests in the course of analysis:

Blue: **Cu** in ammoniacal solution; **Ni** in $(NH_4)_2CO_3$ solution; **I** in presence of starch solution; **HCN**, in very dilute solutions, converted into Prussian Blue; **$H_4Fe(CN)_6$**, in very dilute solution, with Fe_2Cl_6; **$H_6Fe_2(CN)_{12}$**, in very dilute solution, with $FeSO_4$.

Blue-Black: **Gallic** and **Tannic** Acids with Fe_2Cl_6.

Brown: **HNO_3** and **HNO_2** with $FeSO_4 + H_2SO_4$.

Purple (in dilute solution Pink): **Mn** as $H_2Mn_2O_8$; **I** dissolved in $CHCl_3$; **H_2S** (in alkaline sulphides) with Sodium Nitro-prusside.

Red: **HCNS** with Fe_2Cl_6; **Fe** (in Ferric Salts) with KCNS.

Rose-red: **H_2SO_3** in Nitro-prusside test.

Violet: **Salicylic** Acid with Fe_2Cl_6 (permanent); **$H_2S_2O_3$** with Fe_2Cl_6 (transient).

Yellow: **Pt** in $PtCl_2$ (in strong solutions Brown); **Cr** in Na_2CrO_4; **Br** dissolved in $CHCl_3$ (in strong solutions Brown).

C. FLAME TESTS. A piece of platinum wire is mounted in a section of glass tubing by fusing the tubing around one end of the wire; the other end of the wire is bent to form a small loop. Clean the wire by holding it in the colorless Bunsen flame until the latter is no longer colored, a result more rapidly accomplished by moistening the wire with HCl. The cleaned wire is now dipped into the solution, which should be concentrated, or in case a precipitate is to be tested a little of this is removed in the loop, and held in the flame; by moistening the wire with HCl, volatile chlorides are formed, which give more pronounced colorations. The following give flame colorations:

Na, intense yellow; **Ca**, yellowish red; **Sr**, intense red; **Li**, purplish red; **Cu**, blue or green; **Ba**, gray-green; H_3BO_3, green; **K**, violet.

Because of the marked interference of **Na** with the **K** and **Li** colorations, the flame is viewed through sufficient blue glass (generally three pieces are necessary) to entirely obstruct the **Na** and **Li** flames, when **K** causes a purplish-red coloration (organic matter causes a flame coloration, which is also purplish-red, so that this must be first removed by ignition); to detect the **Li**, Li_3PO_4 must be first precipitated, washed until free from **Na** and the precipitate examined *without* blue glass. (See **Eff.**)

D. BORAX BEADS. Mount a piece of platinum wire in glass and bend end of wire to form a circle about 3 mm. in diameter; heat the wire, dip into anhydrous borax, fuse the latter in the flame and add more borax to completely fill the circle; the Borax Bead should be perfectly clear and free from color, otherwise it is melted, thrown out of the wire by a jerk and other beads made until the last one is free from color. A small quantity of the precipitate, or residue from a solution to be tested is caught on the hot bead and heated in the oxidizing flame until perfectly admixed or dissolved in the fused Borax. The following are the most important metals giving characteristic Borax Beads:

	Oxidizing Flame.		Reducing Flame.	
	Hot.	Cold.	Hot.	Cold.
Cu.	Green.	Blue or Greenish-blue.	Red.	Red.
Fe.	Red to Brown.	Yellow.	Green.	Green.
Ce.	Red.	Yellow.	Colorless.	Colorless.
Cr.	Yellow to Red.	Greenish-yellow.	Green.	Green.
U.	Yellow.	Yellowish-green.	Green.	Green.
Mn.	Violet.	Amethyst.	Colorless.	Faint pink.
Ni.	Violet.	Brown.	Opaque, due to separation of Ni.	
Co.	Blue.	Blue.	Blue.	Blue.
Va.	Colorless or yellow.		Brown.	Green.

E. PRODUCTION OF COLORED RESIDUES by heating a small portion of a solid, or the residue left from evaporating a small quantity of solution, upon a porcelain crucible lid:

Black: **CuO, Co_2O_3, Ni_2O_3**, and **C** from non-volatile organic substances; **$Na_2S_2O_3$** frequently yields a black residue.

Black-green: U_3O_8.
Brown-red while hot, reddish-yellow on cooling: **PbO**.
Brown while hot, pale yellow on cooling: **SnO_2**.
Green: **NiO; Cr_2O_3**.
Orange while hot, yellow on cooling: **Bi_2O_3**.
Red-brown: **Fe_2O_3; Mn_3O_4; CdO**.
Red or Pink: **Hypophosphites**, due to separation of amorphous **P**.
Yellow while hot, white on cooling: **ZnO**.

F. PRODUCTION OF COLORED INCRUSTATIONS ON CHARCOAL, by moistening powder with H_2O to form a stiff paste, introducing into cavity on charcoal and heating first gently, later to intense ignition:

Red-brown: **Ag_2O; CdO**.
Dark lemon-yellow while hot, pale yellow on cooling: **PbO**.
Dark orange-yellow while hot, yellow on cooling: **Bi_2O_3**.
Yellow while hot, white on cooling: **ZnO**.
Faint yellow while hot, white on cooling: **SnO_2**.
White: **As_2O_3; Sb_2O_3**.

G. PRODUCTION OF COLORED RESIDUES ON CHARCOAL, after heating in the oxidizing flame, cooling, moistening with $Co(NO_3)_2$ and again strongly heating:

Blue = **Al**; Bluish-green = **Sn**; Green = **Zn**; Pink = **Mg**.

IIIA. VOLATILE PRODUCT SOUGHT FOR:

1. Due to the insolubility of a gas; when a reaction involves the liberation of a gas which cannot be held in solution by the quantity of liquid present, the excess escapes and causes the phenomenon called *effervescence;* as gases are less soluble in hot liquids, their detection is favored by warming the solution before adding the reagent. The following tests illustrate the above division:

H_2CO_3 $= CO_2$; **HNO_2** $= N_2O_3$; **$HClO$** $= Cl$; **$HClO_3$** $= Cl_2O_4$;
H_2SO_3 and **$H_2S_2O_3$** $= SO_2$; **H_2S**; **HCN**; **NH_4** salts $= NH_3$.

2. Due to formation of volatile liquids or solids: as in tests for H_3BO_3, $HC_2H_3O_2$; **Hg, Sb** and **As** result upon heating compounds of these with Na_2CO_3 or KCN in glass tubes closed at one end.

B. NON-VOLATILE PRODUCT SOUGHT FOR:

1. Reduction of Metallic Compounds on charcoal; after mixing with Na_2CO_3, heat in a small cavity on the charcoal in the reducing flame; if the reduced metal is not visible, cut out the charcoal surrounding the cavity, crush in a mortar and wash away the light charcoal, when the metal can be obtained and examined as to color, malleability and action of acids: **Cu, Bi, Sb, Pb, Ag,** etc.
2. Reduction of Metallic Compounds with Na_2CO_3, or KCN heated in small glass tubes closed at one end—**Bi, Ag, Sn, Pb,** etc.
3. Ignition to remove interfering NH_4 salts, as in Groups III and I.

Analytical Chemistry

Is properly divided into two parts:

1. Tests for the **Metals** or **Bases**; and 2. Tests for the **Non-metals** and **Acids.**

Of the two the former is much the easier for a beginner, since it is possible by the systematic use of a few reagents called **group reagents** to precipitate successive groups of metals, and then by the use of other reagents, to determine the metals which are precipitated by the group reagent.

The tests for the Acids are much more complicated, since there are here no group reagents which in their use correspond to those used in the testing of Metals; consequently, the tests for some acids are more or less interfered with by the presence of other acids.

The solutions given for analysis contain under no condition more than 1 per cent. of a salt of each metal or acid to be tested for; in some cases much less is present, so that the student is drilled into careful work, so as to be successful in the analysis of unknown solutions.

Tests for Metals or Bases.

Most of the metals form salts which give colorless solutions; the following are the more important exceptions: **Cu,** blue or green; **Au** and **Pt,** yellow; **Cr** (acid-forming), yellow or orange reduced by HCl and H_2S to **Cr** (base-forming), green or violet; **Mn** (acid-forming), green or purple reduced by HCl + H_2S to **Mn** (base-forming), pink or colorless; **Ferric** salts, yellow or brown reduced by HCl and H_2S to **Ferrous** salts, pale-green or colorless; **Co,** pink; and **Ni,** green.

Whilst the Table of Solubilities shows that many insoluble compounds of the metals are formed, this table does not give sufficient details of the solubilities, as required for analytical work. A special table is, therefore, given in which all of the Important Tests for the Metals are indicated, and the student should be required to take up these tests for each group of metals, note the action in each test, write the involved reactions and submit the records of the tests for inspection.

The following **Key** gives all necessary explanations:

In case two reagents are separated by a (+) sign only, these reagents can be added one after the other, or admixed in case two liquids are to be used.

If they are separated by (; +), the precipitate produced by the first reagent or reagents should be filtered off and washed with H_2O before subjecting it to the reagent or reagents following the (; +).

Lastly, if a reagent is enclosed in ( ), this reagent is only to be used in a test indicated by enclosure in ( ), as (1) or (2).

1. Shows that the metallic salt and reagent respond in forming a Precipitate (insoluble in excess of reagent), Flame-test, Borax Bead, Volatile Substance or Change in Color.
2. Shows that the metallic salt and reagent form a Precipitate soluble in excess of the reagent or reagents.
3. Shows that no change occurs, making an important point of difference between two valences of the same metal, or between two metals of the same group.

Table of Important Tests for Metals.

	Hg$_2$ II	Ag I	Pb II	Bi III	Cu II	Cd II	Sn II	Sn IV	As III	Sb III	Au III	Pt IV	Hg II	Mo	Fe II	Fe$_2$ VI	U	Ce$_2$ VI	Cr$_2$ VI	Al$_2$ VI	Mn II	Zn II	Co II	Ni II	W	Va	Ba II	Sr II	Ca II	Mg II	K I	Na I	Li I	NH$_4$ I
Dil. HCl	1	1	1	2						2															1									—
Dil. HCl + H_2O	1	1	2	1						1																								—
Dil. HCl; + NH_4OH	1	2	1																						2									—
H_2S + Dil. HCl	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	2								2	2								—
H_2S; + HCl 1·12						2	2	2		2																								—
H_2S; + HNO_3 1·20			2	2	2	2			2																									—
H_2S; + Aq. Regiæ									2		2	2	2																					—
H_2S + KCN					2	1																												—
H_2S; + $(NH_4)_2CO_3$									2																									—
$Na_2S + NaOH$		1	1	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1	1	2	1	1	1	1	2	2								—
$H_2S + NH_4OH$		1	1	1	1	1	2	2	2	2	2	2	1	2	1	1	1	1	1	1	1	1	1	1	2	2								—
$NH_4OH + NH_4Cl$	1	2	1	1	2	2	1	1		1			1		1	1	1	1	1	1	2	2	2	2						2				—
KOH or NaOH	1	1	2	1	1	1	2	2		2			1		1	1	1	1	1	2	1	2	1	1						1				1
NaOH + NaClO;			1												1	1		1	2	2	1	2	1	1										—
+ $(NH_4)_2CO_3 + C_2H_6O$																					1	2	1	2										—
$(NH_4)_2CO_3$ + (NH_4Cl)		2	1	1	2	1									1	1	2	1	1	1	2	2	2	2		(1)	1	1	1	(2)				—
Na_2CO_3	1	1	1	1	1	1	1	1		1			1		1	1		1	1	1	1	1	1	1			1	1	1	1				1
$(NH_4)_2HPO_4 + NH_4OH$		2	1		2										1	1		1	1	1	2	2	2	2			1	1	1	1				—
$Na_2HPO_4 + NaOH$			2		1															2	1	2	1	1			1	1	1	1			1	—
Dil. H_2SO_4			1					1																			1	1	1	3				—
K_2CrO_4 + HA	1	1	1	1									1														1	3						—
$H_2C_2O_4$ + Dil. H_2SO_4											1							1											2					—
$(NH_4)_2C_2O_4 + HC_2H_3O_2$			1		1													1									2	1	1	2				—
$(NH_4)_2C_2O_4 + NH_4OH$			1		2																						1	1	1	2				—
$K_4Fe(CN)_6$		1			1										1	1	1					1												—
$K_6Fe_2(CN)_{12}$		1													1	1																		—
KCNS + $(HgCl_2)$	1	1			1								3		3	(1)																		—
$SnCl_2$ + HCl	1								1	1	1	1	1	1		1									1									—
$FeSO_4$											1																							—
$HgCl_2$							1																											—
KI	1	1	1	2	1								2			1																		—
$PtCl_4$																															1	3	3	1
$HNO_3 + Pb_3O_4$																					1													—
Fe + HCl	1	1			1					1	1		1																					—
Sn + HCl									1	1				1											1									—
Cu + HCl	1			1					1	1			1																					—
Zn + H_2SO_4 dil.									1	1				1											1									—
Zn + KOH									1	1																								—
Flame test					1																						1	1	1		1	1	1	—
Borax bead					1										1	1	1	1	1		1		1	1		1								—
Heated on porcelain	1		1	1	1	1			1	1			1			1	1		1		1	1	1	1										1
Heated on charcoal;		1	1	1	1	1	1		1	1				1											1									—
+ $Co(NO_3)_2$							1	1												1		1								1				—
Heated with Na_2CO_3	1	1											1				2				2			1	2	2								1
Heated with KCN		1	1	1			1	1	1	1																								—

It will be noticed that only a comparatively small number of these tests lend themselves to a systematic course of analysis. The examination of an unknown solution necessitates the use of the **group reagents** in the following order:

Action of Group Reagents.

Dilute HCl, precipitates Group VII as white Hg_2Cl_2, AgCl and $PbCl_2$; the last being somewhat soluble in H_2O explains the presence of Pb in the following group.

The filtrate from the HCl precipitation contains Groups I–VI; from this

H_2S, in presence of not too great an excess of **dil. HCl,** precipitates Groups V–VI, as black PbS, HgS and CuS; brownish-black Au_2S_3 and PtS_2; brown Bi_2S_3 and SnS; orange-red Sb_2S_3; yellow As_2S_3, SnS_2 and CdS. By treating this precipitate with Na_2S and NaOH, Group VI containing Pb, Bi, Cu and Cd is left insoluble, while Group V containing Hg (ic), Au, Pt, As, Sb and Sn is dissolved.

The filtrate from the above H_2S precipitation contains Groups I–IV, from which

H_2S, after making faintly alkaline with **NH_4OH,** precipitates Groups III–IV, yielding black FeS, CoS and NiS; green $Cr_2(OH)_6$; pink MnS; white $Al_2(OH)_6$, $Ce_2(OH)_6$ and ZnS. This precipitate dissolved in Aq. Regiæ is separated by adding NH_4OH in excess into insoluble Group IV yielding brown $Fe_2(OH)_6$, green $Cr_2(OH)_6$ and white $Ce_2(OH)_6$ and $Al_2(OH)_6$, and into soluble Group III containing $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$ and $Zn(OH)_2$.

The filtrate from the ammoniacal H_2S precipitation contains Groups I–II, from which

$(NH_4)_2CO_3$ precipitates white $BaCO_3$, $SrCO_3$ and $CaCO_3$; $MgCO_3$ is held in solution by the presence of ammonium salts, especially NH_4Cl, so that for Mg and the alkalies, present in the filtrate from the $(NH_4)_2CO_3$ precipitation, special tests must be made:

Mg use $(NH_4)_2HPO_4$ and NH_4OH precipitates $MgNH_4PO_4$;

K, Li and Na by flame test after ignition to remove NH_4 salts and organic matter;

Li in presence of Na by precipitation with Na_2HPO_4 and NaOH.

It is to be noted that in all of the group separations by the main reagents only NH_4 salts are added or formed in the precipitations; this prevents the introduction of non-volatile reagents and allows tests to be made for all metals or metallic groups excepting NH_4 in the one portion of solution taken for the analysis, while for NH_4 a special test must be made in a portion of the original solution as given in the chart.

Analytical Operations.

Before taking up the detailed description of the analysis for metals, a few notes and cautions on some of the operations must be studied.

Addition of Reagents. These must always be added in sufficient quantity to do the work expected of them, the necessary quantity depending upon the amount of the substance to be tested for.

A sufficiency of some reagents can be told by the odor after thorough agitation, as in the case of H_2S and NH_4OH; some by the color of the supernatant liquid, as with K_2CrO_4; some by action upon red litmus paper, as in the addition of NaOH in the NH_4 test, or upon blue litmus paper, as in the addition of HNO_3 in the Ag test.

In some cases it is necessary to add an *excess* of a reagent for the purpose of *redissolving* a precipitate which was formed by the first additions of the same reagent. This is a very important step in the analysis of Groups III and IV where NH_4OH or NaOH is directed to be added in excess; in cases of this kind the reagent must be added until after thorough admixture, an alkaline reaction is noted, and then an additional quantity added which constitutes the excess.

In all cases where the above indications do not apply, and especially in the case of the group reagents, it is a good plan to allow the precipitate to settle and add more reagent to the clear supernatant liquid before filtering, and after filtering to test the filtrate with a little more reagent so as to be absolutely sure that the work up to that point has been carried out properly.

FILTRATION. If the addition of a reagent produces a precipitate, the mixture must be filtered through a plain filter, so adjusted in the funnel that the upper part fits snugly, while the lower part hangs free; the filter should be wetted with water and the folds pressed down to prevent the precipitate from getting in back of the folds. The precipitate is retained in the filter while the filtrate passes through; if the latter runs through turbid it will have to be returned to the filter until it runs through clear.

WASHING OF PRECIPITATES. Always wash with two small portions of water, unless some other liquid is directed, allowing these to run into the filtrate, thus avoiding loss of the metals still to be tested for; hot water can generally be used, excepting when cold water is especially mentioned. Finally wash with a larger quantity of water, and throw this away. In pouring on these portions of liquid see that the entire filter and precipitate gets its share.

TREATMENT OF PRECIPITATES WITH REAGENTS. This in all cases can be done directly upon the filter after washing; the reagent, heated in a test tube if necessary, should be poured in such a way as to cover all parts of the filter as well as the precipitate; allow to run through, warm and again return to filter and precipitate; repeat a third time and then wash with water, as directed above.

FLAME, BORAX-BEAD, CHARCOAL and IGNITION TESTS have been explained on pages 16 and 17

IGNITE may mean to drive off volatile matter by heating and without the material burning, as in the removal of NH_4 salts, or to set on fire, as in the test for Boric Acid.

Notes on the Scheme for the Separation of Bases.

In this "**Scheme**" pages 28 to 30, letters and combinations of letters are used to indicate every step of the analytical operation; the final letter **p** stands for precipitate or insoluble compound, the letter **f** for filtrate or that part running through the filter. In the examination of a precipitate each operation, to which the precipitate is subjected, is indicated by an additional letter, **p** for the insoluble and **f** for the soluble part.

If a reagent produces no precipitate, filtration is unnecessary, and the solution takes the next letter in the alphabet with a final **f**.

A. 5 cubic centimeters of any solution, an ample quantity for the analysis for bases, are tested with litmus paper to determine if acid or alkaline; if alkaline, acidify with **dilute HCl** and then add 5 cubic centimeters more: if no precipitate is produced, Group VII is absent (with exception of Pb, which will be found in Group VI), proceed according to **Bf**.

If a precipitate is produced, collect upon a filter (= **Bp**) and wash with cold H_2O; filtrate and washings (= **Bf**).

In presence of Bi and Sb salts, **dil. HCl** in small quantity may cause a precipitate of BiOCl and SbOCl, which are soluble, however, in the excess of dil. HCl. Solutions of SnO, SnO_2, ZnO and $Al_2(OH)_6$ in excess of KOH or NaOH will, upon neutralization with HCl, give precipitates of the Hydrates of these metals, soluble in an excess of HCl. Sulphides of Group V dissolved in $Na_2S + NaOH$, and As_2S_3 dissolved in alkaline carbonates will be precipitated upon acidifying with dil. HCl, insoluble in excess of dil. HCl; these sulphides are, however, colored and not white.

Acid solutions of Sn salts, after a time, deposit SnO_2, which is difficultly soluble in **dilute HCl** and may be filtered out in Group VII, and therefore missed in the analysis.

A number of acids are liberated or decomposed by the addition of **dil. HCl** to salts of these acids, causing effervescence, odor or precipitates; the list of these acids is given under Acids, Rule II, where dil. H_2SO_4 is the reagent, but dil. HCl brings about the same results. Benzoic, Salicylic and Gallic Acids being soluble in hot H_2O, may work out as Pb in **Bpf**, but always separate from hot solution in crystalline needles, whereas $PbSO_4$ separates as a fine white precipitate.

Solutions containing Ba or Sr may give slight precipitates with dil. HCl, containing traces of H_2SO_4; if these be filtered out and the filter not thoroughly washed, the hot H_2O used to extract Pb(**Bpf**) will give a fine white precipitate of $BaSO_4$ or $SrSO_4$. Therefore, a test for Pb in Group VII must be confirmed by a test in Group VI, where Ba and Sr will not interfere.

Bp. Treat precipitate on filter with 5 cubic centimeters boiling H_2O to remove $PbCl_2$ (AgCl and Hg_2Cl_2 are insoluble = **Bpp**) wash with H_2O and test the filtrate = **Bpf** for Pb by adding 5 cubic centimeters dil. H_2SO_4, and allowing to stand ten minutes.

Bpp. Treat on filter with dil. NH_4OH (5 per cent. NH_3): AgCl is dissolved = **Bppf**; Hg_2Cl_2 is immediately blackened, due to formation of Hg_2NH_2Cl = **Bppp.**

Bppf. Test for Ag by acidifying with dilute HNO_3; solution must be *acid* before AgCl is reprecipitated.

Bf. Add NH_4OH (10 per cent. NH_3) until neutral or faintly alkaline, then dilute HCl, drop by drop, until solution after thorough mixing is slightly acid, then add about 2 cubic centimeters more of dil. HCl, warm, pass in **H_2S** until solution smells strongly of H_2S after thorough shaking. If no precipitate is produced, proceed according to **Cf.**

If a precipitate is produced, set aside for five to ten minutes, and pass in more H_2S; be sure that the mixture smells strongly of H_2S after thorough agitation, before filtering off the precipitate and test filtrate with more H_2S. If a further precipitate is produced, collect upon the same filter and test filtrate again with H_2S until perfectly precipitated, then wash with warm H_2O. Filtrate and washings = **Cf**; precipitate = **Cp.**

The above directions for preparing the solution for the H_2S precipitation are extremely important, for if the solution be *alkaline* H_2S will precipitate Groups VI, III and IV, while Group V will remain in solution; if an insufficient quantity of HCl be present, some of the members of Groups III–IV will be precipitated with Groups V–VI; lastly, if too much **dil. HCl** be present some members of Groups V–VI will not be precipitated, or at best but incompletely, and will later appear in the precipitate of Groups III–IV. In any one of these three cases it is apparent that wrong results must be obtained.

H_2S with Hg(ic) salts gives first a white precipitate of a mixed compound, $HgCl_2$, for instance, giving ($HgCl_2$, HgS); more **H_2S** changes this into black HgS. Pb salts in strongly acid solution give a red precipitate, slowly becoming black PbS. Arsenic compounds are reduced to arsenous, and slowly yield a precipitate of $As_2S_3 + S_2$.

That the precipitation of Group VII with **dil. HCl** is very desirable before precipitating Groups V–VI with **H_2S** can be seen from the behavior of Hg_2 and Ag salts with H_2S. Hg_2S decomposes into Hg and HgS, the latter in subsequent operations passing into Group V, the former remains in Group VI, dissolving in HNO_3, and interfering with the tests for the metals of Group VI; Ag_2S is but slightly acted upon by HNO_3 (1.20), hence, most of the Ag will be found in **Cppp**, but the small quantity which dissolves will precipitate with Cd.

H_2S in acid solutions, prepared according to **Bf**, will not precipitate metals of Groups III–IV, but it will reduce Ferric salts to Ferrous, Manganic and Permanganic salts to Manganous, and Chromates to base-forming Chromic salts; all of these reductions are attended by separation of **S.** A number of acids are also reduced by **H_2S**, and Cl, Br and I react with **H_2S** with separation of **S**; see Reactions Based on Oxidation and Reduction, page 10.

Cp. Treat on filter with a warm mixture of 5 cubic centimeters, each of **Na_2S** and **NaOH**: Group V forms soluble sulpho-salts, but traces of Hg(ic), Au and Pt are prevented from dissolving by the presence of sulphides of Group VI. Na_2S + **NaOH** solution and washings = **Cpf**; insoluble part on filter = **Cpp.**

Cpp. Treat with 5 cubic centimeters, boiling HNO_3 (Sp. gr. 1.20); this will dissolve the sulphides of Pb, Bi, Cu and Cd, forming nitrates with separation of S which remains on filter with traces of Hg(ic), Au and Pt = **Cppp**; filtrate and washings = **Cppf.**
The treatment with HNO_3 must be repeated three times by boiling the filtrate and returning to the filter, covering all parts of the filter and precipitate.
If dil. HNO_3 (5 per cent.) be used for the above treatment, the sulphides of Group VI will not be dissolved; if a more concentrated HNO_3 (1.42) be used, this will oxidize the sulphides to sulphates and $PbSO_4$ will remain on the filter.

Cppp. Wash thoroughly to remove soluble nitrates of Group VI, and use the filter later for collecting **Cpfp**; by so doing the filter will contain everything belonging to Group V, and insure better tests for Au and Pt especially.

Cppf. Add NH_4OH in excess, until a strong odor of NH_3 persists after thorough mixing; then boil for several minutes, either in a test-tube or, if there is too much solution for this, in a beaker. The hydrates of the metals are here formed, of which Cd and Cu = **Cppff** are easily soluble in excess. Bi is precipitated at once, but Pb first forms a basic salt, which is somewhat soluble and requires the boiling for its precipitation = **Cppfp,** otherwise a black or, at least, dark-colored precipitate is later obtained in the test for Cd.

Cppff. The formation of the blue solution is one of the most delicate tests for Cu; to detect Cd, KCN is added to decolorize the blue solution by forming a colorless potassium-cuprous cyanide, which does not yield CuS on addition of H_2S and does not prevent the precipitation of yellow CdS.

Cppfp. The hydrates of Bi and Pb readily dissolve in 2 cubic centimeters boiling dil. HCl; this solution is evaporated just to dryness in a test-tube, the last portions of HCl removed by blowing into the tube and then 5 to 10 cubic centimeters H_2O added: $BiCl_3$ is decomposed into insoluble BiOCl forming a white milky mixture, while $PbCl_2$ dissolves and is tested for in the filtrate from the BiOCl by adding 5 cubic centimeters dil. H_2SO_4. If Pb is present in a solution, a precipitate of $PbSO_4$ must be formed in this test.

Cpf. As stated before Group V dissolves in **Na_2S + NaOH** by reason of forming soluble sulpho-salts as Na_3AsS_3, Na_2HgS_2, etc.; by acidifying this solution with dil. HCl the Na_2S + NaOH are decomposed and the original sulphides reprecipitated. By collecting this precipitate on the filter containing **Cppp** everything belonging to Group V is re-combined. **Cpff** contains only NaCl and H_2S and is to be thrown away.

Cpfp. Treat on filter with 5 cubic centimeters boiling concentrated HCl (sp. gr. 1.12). This dissolves the sulphides of Sb and Sn with liberation of H_2S = **Cpfpf** and should be boiled to expel H_2S every time before returning to the filter; the sulphides of Hg (ic), Au, Pt and As = **Cpfpp** are insoluble in HCl.

Cpfpf. Contains $SbCl_3$ and $SnCl_2$ or $SnCl_4$. Boil to expel H_2S, as this may stain the Sn used for the Sb test; dilute with H_2O and divide into 2 parts:

a. Add a small section of Sn foil, a black stain (due to a deposit of metallic Sb on the Sn) = Sb.

b. Add a bunch of Fe wire (card teeth), warm to start the liberation of H, which reduces $SnCl_4$ to $SnCl_2$, allow to stand ten minutes, filter out the excess of Fe (and the precipitated Sb) and pour a little of the solution into some $HgCl_2$; the $SnCl_2$ in reducing $HgCl_2$ to insoluble Hg_2Cl_2 is oxidized to $SnCl_4$; if an excess of $SnCl_2$ is added, gray metallic Hg will be precipitated.

Cpfpp. Treatment with $(NH_4)_2CO_3$ removes As_2S_3 as $(NH_4)_3AsS_3$ + $(NH_4)_3$ AsO_3 = **Cpfppf,** which on *acidifying* with dil. HCl (do not shake in a closed test-tube on account of pressure by the evolved CO_2, but pour from one test-tube into another) reprecipitates As_2S_3; unless traces of As are to be looked for, the H_2S need not be added.

Cpfppp. Mix 4 cubic centimeters conc. HCl (1.12) and 1 cubic centimeter HNO_3 (1.20), warm and pour over precipitate and filter, return as long as any action is noticeable; this dissolves Hg (ic) and most of the Au and Pt, but some of the latter are protected by the liberated S; wash with a little H_2O, and set filtrate and washings aside; wash filter thoroughly to remove all traces of the Aq. Regiæ, fold the filter and hold it, by means of a Pt wire mounted in glass, in the Bunsen flame until it becomes dry and chars; continue heating to burn off as much C as possible, and drop the ash into the Aq. Regiæ solution; evaporate in a test-tube until about 6 to 8 drops are left, cool, add 5 cubic centimeters dil. HCl and filter (disregard this filter). Add a small crystal of $FeSO_4$ and allow to dissolve; in presence of Au the solution becomes more or less turbid, due to the separation of metallic Au; filter through a small filter, adding but a few drops of the solution at a time so as to collect all of the precipitate in the lower part of the filter; if necessary, run the filtrate through the filter a second time, and then wash: a blue stain on the filter = Au.

Cpfpppf. Contains Hg (ic) and Pt; add $SnCl_2$ drop by drop until finally about 3 cubic centimeters are added: a white precipitate turning gray = Hg (ic); filter through a small filter as described in the test for Au: yellow or brown filtrate = Pt. In absence of Pt a colorless filtrate results. The last tests depend upon the change of $SnCl_2$ into $SnCl_4$: $HgCl_2$ is reduced to Hg_2Cl_2 and finally to Hg; $PtCl_4$ to $PtCl_2$, which has intense tinctorial power.

Cf. Add **NH_4OH** (10 per cent. NH_3) until faintly alkaline and saturate with **H_2S**: If no precipitate is formed, proceed to **Df**; if a precipitate is formed, collect upon a filter and test filtrate at once with more H_2S; if no further precipitate is produced, wash filter containing precipitate with hot H_2O. Filtrate and washings = **Df**; precipitate = **Dp**.

The action of **NH_4OH** and **H_2S** in the above directions practically result in forming **$(NH_4)_2S$** or **NH_4HS** as the precipitant; if not too much free NH_4OH is present before passing in H_2S, very little $(NH_4)_2S$ or NH_4HS can be present in the solution, which is a distinct advantage, since an excess of this reagent redissolves NiS, and this passes into **Df**, causing a brown filtrate.

In the presence of *non-volatile organic substances* like tartaric and citric acids, sugar, etc., those metals of Group IV which do not form sulphides (Al, Cr and Ce) are not precipitated, or but imperfectly, by NH_4OH and H_2S. In such cases **Cf** must be evaporated to dryness, the residue ignited to destroy the interfering substances, redissolved in HCl and proceeded with.

In the presence of oxalic, phosphoric, boric and hydrofluoric acids, which form salts with the metals of Group II soluble in the stronger mineral acids, the addition of NH_4OH to alkaline reaction causes the precipitation of Group II with Groups III–IV. The most important exception of this kind is with H_3PO_4, for which the necessary changes in the analysis are given in the **Phosphate Chart.** See pages 26 and 31.

Dp. Treat with a hot mixture of 4 cubic centimeters HCl (1·12) and 1 cubic centimeter HNO_3 (1·2), by pouring repeatedly over the filter and precipitate; this should dissolve almost the entire precipitate (leaving a gummy mass of S, which retains a little CoS or NiS, or both, and which after washing is to be tested by the Borax Bead).

The acid solution and washings are evaporated in a test-tube to a very small bulk, diluted with H_2O (HCl should only be necessary in presence of H_3PO_4 to dissolve the residue from evaporation) and NH_4OH (10 per cent.) added in excess (until strong odor of NH_3 after mixing); collect on filter and wash with hot H_2O: Filtrate and washings = **Dpf**; precipitate = **Dpp.**

Aqua Regiæ is used to dissolve **Dp** because CoS and NiS are not readily dissolved by HCl, and to insure the oxidation of iron to the ferric state.

NH_4OH forms hydrates of the metals of Groups III and IV, of which those of Group III are soluble in excess, those of Group IV and (in presence of H_3PO_4) the phosphates of Group II are insoluble.

Mn normally belongs to Group III, but the tendency of $Mn(OH)_2$ to take up O and change to a manganic compound which is insoluble in NH_4OH, partly accounts for its presence in Group IV; there is a marked affinity of $Mn(OH)_2$ for the hydrates of Group IV so that Mn is always found in Group IV if members of the latter group are present.

Dpp. If H_3PO_4 is suspected, test a small portion of the precipitate according to **Phosphate Chart** for H_3PO_4; dissolve the balance of this precipitate in 5 cubic centimeters dil. HCl, add sufficient NaOH to give an alkaline reaction after thorough mixing, then add 5 cubic centimeters more of NaOH and 5 cubic centimeters of NaClO, boil in a beaker for several minutes (alkaline solutions are boiled with difficulty in test tubes, due to an irregular boiling or bumping, which causes loss of the solution). Filtrate and washings = **Dppf**; precipitate = **Dppp.**

NaOH precipitates the hydrates of the metals of Group IV, of these $Al_2(OH)_6$ is soluble in excess of NaOH; the NaClO by boiling oxidizes $Cr_2(OH)_6$ to H_2CrO_4, which is also soluble in NaOH; $Fe_2(OH)_6$ is unchanged, while $Ce_2(OH)_6$ and $Mn(OH)_2$ are oxidized to $Ce(OH)_4$ and $Mn(OH)_4$. To effect these changes it is essential to boil for several minutes, otherwise Cr will remain with **Dppp.**

Dppp. Test for Mn: A very small quantity of the precipitate is boiled with 5 cubic centimeters dil. HNO_3, and Pb_3O_4 added in small quantities until a little of this remains insoluble; then allow to stand until the precipitate settles perfectly: a purple or pink supernatant liquid = Mn. This is Crum's test, and depends upon the formation of $H_2Mn_2O_8$.

Treat the balance of **Dppp** with 5 cubic centimeters boiling dil. H_2SO_4: filtrate and washings = **Dpppf** (Fe and Ce); precipitate **Dpppp** = $Mn(OH)_4$, insoluble in dil. H_2SO_4.

Dpppf. Dissolve a few small crystals of Oxalic Acid in this filtrate by heating, and then allow to cool: a white crystalline precipitate of cerium oxalate, almost insoluble in dil. H_2SO_4; filter and test filtrate for Fe, which at this stage is always present as ferric salt, hence, Tests for **Fe** in the original solution must be made to determine if present as **Fe(ous)** or **Fe(ic)** salts, or both. For this purpose $K_4Fe(CN)_6$ and $K_6Fe_2(CN)_{12}$ constitute the most reliable tests, the former reagent, Potassium *Ferro*cyanide, giving with Fe(ic) salts a a dark blue precipitate, while the latter, Potassium *Ferri*cyanide, gives with Fe(ous) salts a dark blue precipitate; all other colored precipitates are disregarded, as these are due to other metals, as is shown in the following:

	Fe(ous)	**Fe(ic)**	**Mn**	**Co**	**Ni**	**Cu**
$K_4Fe(CN)_6$	bluish white	dark blue	reddish	green	greenish white	red brown
$K_6Fe(CN)_{12}$	dark blue	brown color	brown	brown red	yellowish brown	yellowish green

Dppf. Yellow, if Cr be present. Acidify with Acetic Acid, boil to expel Cl (from NaClO), divide and test for: **Al,** by adding Na_2HPO_4 and boiling: a white gelatinous precipitate of $Al_2(PO_4)_2$ insoluble in Acetic Acid.

Cr, by adding a few drops Lead Acetate: an immediate yellow precipitate of $PbCrO_4$ insoluble in Acetic Acid. In the absence of Cr a white precipitate generally forms, which after standing will gradually turn yellow, orange and finally brown, due to the action of unexpelled Cl upon lead salts; for this reason, only an *immediate* yellow precipitate = Cr.

Dpf. Evaporate to dryness in an evaporating dish, ignite to remove NH_4 salts (which interfere with the oxidation by NaClO), cool; treat residue with 2 cubic centimeters hot dil. HCl, transfer to a small beaker, add NaOH until *alkaline* after mixing, then 5 cubic centimeters more NaOH (to dissolve $Zn(OH)_2$), and 5 cubic centimeters NaClO, boil for several minutes, filter and wash: Filtrate and washings = **Dpff**; precipitate = **Dpfp.**

The excess of NaOH dissolves Zn; the hydrates of Mn, Co and Ni are insoluble in NaOH, but on boiling with NaClO are oxidized to $Mn(OH)_4$, $Co_2(OH)_6$ and $Ni_2(OH)_6$ if this oxidation is not perfect, difficulty will be experienced in testing for Ni.

Dpff. $Na_2S_2O_3$ is added (2 cubic centimeters) to destroy any excess of NaClO which with H_2S will cause a white precipitate of S; ZnS forms a white flocculent precipitate insoluble in NaOH.

Dpfp. Treat repeatedly on filter with 5 cubic centimeters $(NH_4)_2CO_3$ and 5 drops alcohol; $Ni_2(OH)_6$ is reduced by the alcohol to $Ni(OH)_2$, which is readily soluble in $(NH_4)_2CO_3$. Co and Mn, if thoroughly oxidized, are not dissolved in this treatment. Filtrate = **Dpfpf**; precipitate = **Dpfpp.**

Dpfpf. In addition to the final Borax Bead test, Ni is indicated by the blue or greenish-blue solution and, after adding H_2S and filtering out black NiS, a brown filtrate due to the slight solubility of NiS in $(NH_4)_2S$.

Dpfpp. Test for Co with Borax Bead; for Mn see **Dppp.**

Df. Boiling filtrate and washings is here necessary to prevent a possible precipitation of S and NiS being mistaken for a Group II precipitate, and also to concentrate the solution. If a precipitate is produced, filtration is necessary. To the clear solution add 3 cubic centimeters $(NH_4)_2CO_3$; boil to change the somewhat soluble, amorphous, flocculent carbonates into insoluble crystalline carbonates. If no precipitate forms proceed to **Ef**; if a precipitate forms allow it to subside and add a little more $(NH_4)_2CO_3$ to the supernatant liquid; if a further precipitate forms, boil and add more $(NH_4)_2CO_3$; filter, wash precipitate with hot water; filtrate and washings = **Ef**; precipitate = **Ep.**

$(NH_4)_2CO_3$ precipitates, as already explained, $BaCO_3$, $SrCO_3$ and $CaCO_3$; $MgCO_3$ is retained in solution by the presence of NH_4Cl produced in **Bf** and **Cf** by neutralizing HCl with NH_4OH.
$(NH_4)_2CO_3$ added to an original solution would precipitate all of the metals of previous groups, with the exception of As, Au and Pt, either as carbonates or hydrates, those of Ag, Co, Cd, Mn, Ni and Zn being soluble in excess of $(NH_4)_2CO_3$.

Ep. Acetic Acid dissolves to form acetates; add K_2CrO_4 until the solution is yellow; in absence of Ba, a few drops will suffice to do this = **Epf;** in presence of Ba, sufficient must be added to give a yellow color to the supernatant liquid: filtrate = **Epf**; precipitate = **Epp** or Ba.

Epf. Add 5 centimeters dil. H_2SO_4, and allow to stand for ten minutes; if no precipitate forms proceed to **Epff**; if a precipitate forms this may be either a fine white precipitate, characteristic of Sr, or a course crystalline precipitate of $CaSO_4$, which dissolves on washing with H_2O.

Epff. NH_4OH is needed to neutralize the dil. H_2SO_4, which otherwise would keep CaC_2O_4 in solution; this CaC_2O_4 is insoluble in NH_4OH and in Acetic Acid.

Ef. Concentrate filtrate and washings to the volume of the original solution used, cool and add ¼ volume of NH_4OH(10 per cent. NH_3) and 2 cubic centimeters $(NH_4)_2HPO_4$; stir, allow precipitate to subside and add a little more $(NH_4)_2HPO_4$; if no further precipitate forms filter off the $MgNH_4PO_4$.

Eff. After ignition to remove NH_4 salts, dissolve the residue in two cubic centimeters H_2O and 5 drops dil. HCl and proceed as stated in chart.

Notes on the Phosphate Chart.

Ba, Sr, Ca and Mg in presence of *sufficient* H_3PO_4 will be entirely precipitated with Group IV; if *insufficient* H_3PO_4 is present to combine with all of these metals, part may precipitate with Group IV, part may precipitate in Group II. Therefore, the analysis of Group II must never be neglected in presence of H_3PO_4.

Of the reagents used in **Dpp,** NaClO has no action on phosphates; NaOH, however, may abstract H_3PO_4 from Fe, Ce, Mn and Cr phosphates, forming the hydrate of these metals, so that **Dppp** will consist of $Fe_2(OH)_6$, $Ce(OH)_4$, $Mn(OH)_4$, $Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$. Treatment with boiling dil. H_2SO_4 and washing gives **xDpppp** as the precipitate and **xDpppf** as the filtrate.

xDpppp. Consists of $Mn(OH)_2$, $BaSO_4$ and $SrSO_4$; by treatment with warm $(NH_4)_2CO_3$ the first two are unchanged, the last changed to $SrCO_3$; throw away the $(NH_4)_2CO_3$ solution and washings. Treat precipitate on filter with Acetic Acid and wash : Solution =**xDppppf**; precipitate = **xDppppp,** contains Mn and most of the Ba.

xDppppf. Add a few drops of K_2CrO_4 to give a yellow color; only the slightest precipitate of Ba will be produced; filter.

xDppppff. Add dil. H_2SO_4 and test precipitate for Sr by flame test.

xDpppf. Contains sulphates of Fe, Ce, (Mn?), Ca and Mg with a little H_3PO_4 : add 2 cubic centimeters Na_2HPO_4 (to insure precipitation of Fe and Ce as phosphates), make alkaline with NaOH; then add 5 cubic centimeters each of NaOH and NaClO, to insure oxidation of Mn to $Mn(OH)_4$, boil for several minutes, acidify with acetic acid, boil and filter.

xDpppfp. Contains $Mn(OH)_4$ and phosphates of Fe and Ce, insoluble in Acetic Acid; treat in same manner as **Dppp.**

xDpppff. Contains phosphates of Ca and Mg, soluble in Acetic Acid. Add $(NH_4)_2C_2O_4$ to precipitate Ca as CaC_2O_4, insoluble in Acetic Acid.

xDpppfff. Treat as **Ef** for Mg.

The Analysis of Solutions Containing only Part of the Groups.

For Group VII : Start at **A**; as **Bf** can only contain Pb, add dil. H_2SO_4; **Bp** is treated as described.

For Group VI : Start at **Bf**; **Cf** is disregarded, and **Cp** is taken to **Cpp.**

For Group V : Start at **Bf**; **Cf** is disregarded, and **Cp** is taken to **Cpfp.**

For Group IV : (1) Add 5 cubic centimeters NH_4Cl (to take the place of dil. HCl and NH_4OH used in **A** and **Bf**) and start at **Cf.**
(2) Start at **Dpp** by adding NaOH and NaClO.

For Group III : (1) Add 5 cubic centimeters NH_4Cl (to take the place of dil. HCl and NH_4OH used in **A** and **Bf**) and start at **Cf.**
(2) Start at **Dpf** by adding NaOH and NaClO.

In solutions containing Mn, a portion may be oxidized by the NaClO to permanganate or manganate, causing a purple or green filtrate **Dpff**; to avoid the precipitation of Mn in the Zn test, add a few drops of alcohol to the filtrate, shake and filter through a new filter, disregarding the very slight precipitate on the latter.

For Group II : Add 5 cubic centimeters NH_4Cl, make faintly alkaline with NH_4OH and precipitate with $(NH_4)_2CO_3$ as given in **Df.**

For Group I : Start at **Eff.**

The Exclusion of Some Metals

Means that considerable time can be saved in the analysis, as for example:

Sn excluded: Dilute **Cpfpf** with H_2O and add H_2S: an orange-red precipitate = Sb.

Au and **Pt** excluded: **Cpfppp** contains Hg(ic) as black HgS; dissolve in Aq. Regiæ, evaporate to small bulk, add dil. HCl and $SnCl_2$: a white precipitate turning gray or black = Hg(ic).

Co and **Ni** excluded: Acidify **Dpf** with Acetic Acid and add H_2S: a white precipitate = Zn; filter, test filtrate with more H_2S, then make alkaline with NH_4OH, a pink precipitate = Mn; confirm Mn by testing a little of the precipitate as given in **Dppp.**

Scheme for the Separation of Bases.

A. Groups I–VII. Add dilute HCl until no further effect is noticeable, collect precipitate and wash with cold water.

- **Bp.** Group VII. Hg(ous), Ag, Pb (partly).
- **Bf.** Groups I–VI. To filtrate and washings, add NH_4OH until neutral or faintly alkaline, then dilute HCl until slightly but distinctly acid and pass in H_2S until solution smells strongly after agitation and warming; collect ppt. and wash with hot water.
  - **Cp.** Groups V–VI. Treat upon filter with warm Na_2S and NaOH, and wash.
    - **Cpp.** Group VI. Pb (completely), Bi, Cu, Cd. [Hg(ic), Au, pt.].
    - **Cpf.** Group V. Hg(ic), Au, Pt, As, Sb, Sn.
  - **Cf.** Groups I–IV. Make filtrate and washings *faintly* alkaline with NH_4OH and saturate with H_2S; collect ppt. and wash with hot water.
    - **Dp.** Groups III–IV. Dissolve in as little Aqua Regiæ as possible, wash filter (test any black ppt. left on filter by Borax Bead for Co and Ni); evaporate solution and washings almost to dryness; dissolve in H_2O (and dil. HCl if necessary), add NH_4OH in excess; collect ppt. and wash with hot water.
      - **Dpp.** Group IV. Fe, Ce, Mn, Al, Cr. (and in presence of H_3PO_4 also Ba Sr, Ca, Mg).
      - **Dpf.** Group III. Mn(?), Co, Ni, Zn.
    - **Df.** Groups I–II. Boil filtrate and washings to remove H_2S, and filter, if necessary. Add $(NH_4)_2CO_3$, boil, filter and wash ppt.
      - **Ep.** Ba, Sr, Ca. Dissolve in $H\bar{A}$, wash and add K_2CrO_4 until the solution is yellow; filter.
        - **Epp.** Ba. Yellow ppt.
        - **Epf.** Add dil. H_2SO_4; allow to stand ten minutes; filter.
          - **Epfp.** Sr. Fine white ppt.; wash and confirm by flame test: intense red
          - **Epff.** Ca. Make alkaline with NH_4OH and add $(NH_4)_2C_2O_4$ White ppt.
      - **Ef.** Concentrate filtrate and washings to small bulk, *cool*, add ¼ vol. NH_4OH and some $(NH_4)_2HPO_4$, stir and filter.
        - **Efp.** Mg. White crystalline ppt.
        - **Eff.** Group I. Evaporate to dryness, ignite to remove NH_4 salts; dissolve in H_2O and dil. HCl and try flame tests:
          - *a.* Na intense yellow } without blue-glass.
          - *b.* Li purplish-red } without blue-glass.
          - *c.* K purplish-red through sufficient blue-glass (generally three pieces are needed to obscure Na).

          If the presence of Na obscures the Li flame filter solution, add NaOH and Na_2HPO_4, boil almost to dryness, cool and add dil. NH_4OH: white crystalline ppt.=Li; confirm by flame test after filtering and washing with dil. NH_4OH until *free* from Na.

Test original solution:
For Na by flame test.
For NH_4 by making alkaline with NaOH, heating and noting odor and effect of vapors upon red litmus paper.
For Fe(ous) by adding $K_6Fe_2(CN)_{12}$: dark blue ppt.
For Fe(ic) by adding $K_4Fe(CN)_6$: dark blue ppt.

<table>
<tr><td colspan="3">Bp. Group VII.
Hg(ous), Ag, Pb.
Treat with boiling water.</td></tr>
<tr><td colspan="2">Bpp. Hg(ous), Ag.
Treat with NH_4OH</td><td rowspan="2">Bpf. Pb.
Add dil. H_2SO_4 allow to stand; white ppt.</td></tr>
<tr><td>Bppp. Hg(ous).
Black ppt.</td><td>Bppf. Ag.
Acidify with HNO_3; white ppt.</td></tr>
</table>

<table>
<tr><td colspan="4">Cpp. Group VI.
Pb, Bi, Cu, Cd (Hg(ic), Au, Pt). Treat with boiling HNO_3 (sp. gr. 1·20); wash.</td></tr>
<tr><td rowspan="3">Cppp. Hg(ic) Au, Pt.
Thoroughly wash filter and use for collecting Cpfp.</td><td colspan="3">Cppf. Pb, Bi, Cu, Cd.
Add NH_4OH in excess, <i>boil for several minutes</i>, filter and wash.</td></tr>
<tr><td colspan="2">Cppfp. Pb, Bi.
Dissolve in boiling dil. HCl; evaporate solution to dryness in test-tube; add H_2O.</td><td>Cppff. Cu, Cd.
<i>If blue</i>, Cu is present, add KCN to decolorize, and then H_2S: a yellow ppt.=Cd.
<i>If colorless</i>, Cu is absent; add H_2S for Cd.</td></tr>
<tr><td>Cppfpp.
White turbidity or ppt. Bi.</td><td>Cppfpf.
Add dil. H_2SO_4, allow to stand; white ppt. Pb.</td><td>When directions are not carefully followed in Cppf., a black ppt. may be obtained for Cd; collect this upon a filter, wash and treat with boiling dil. H_2SO_4 dilute with H_2O and add H_2S: a yellow ppt.=Cd.</td></tr>
</table>

<table>
<tr><td colspan="5">Cpf. Group V. Hg(ic), Au, Pt, As, Sb, Sn. Acidify with dil. HCl; collect on filter containing Cppp. and wash.</td></tr>
<tr><td colspan="4">Cpfp. Hg(ic), Au, Pt, As, Sb, Sn.
Treat with boiling conc. HCl; wash.</td><td rowspan="4">Cpff.
Throw away.</td></tr>
<tr><td colspan="3">Cpfpp. Hg(ic), Au, Pt, As.
Treat with $(NH_4)_2CO_3$; wash.</td><td rowspan="3">Cpfpf. Sb, Sn.
Boil to expel H_2S, dilute with H_2O and divide into two parts:
Cpfpfa. Add a fragment of Sn and allow to stand; a black stain upon Sn=Sb.
Cpfpfb. Add metallic Fe, warm, allow to stand ten minutes, filter and pour a little of the solution into some $HgCl_2$: a white ppt.=Sn.</td></tr>
<tr><td colspan="2">Cpfppp. Hg(ic), Au, Pt.
Treat with Aq. Reg.; wash, burn filter and allow ash to drop into Aq. Reg. solution; evaporate almost to dryness, dissolve in dil. HCl and filter. To filtrate (yellow if Au or Pt is present) add a small crystal of $FeSO_4$; filter.</td><td rowspan="2">Cpfppf.
Acidify with dil. HCl and add H_2S; yellow ppt.=As.</td></tr>
<tr><td>Cpfpppp.
Blue or brown ppt.=Au.</td><td>Cpfpppf.
Add $SnCl_2$ in excess; a white ppt. turning gray or black=Hg(ic); filter: a brown filtrate=Pt.</td></tr>
</table>

Dpp. Group IV. Fe, Ce, Mn, Al, Cr.

Dissolve in a little hot dil. HCl, wash filter and add to solution an excess of NaOH, then NaClO, *boil for a few minutes*, and filter.

Dppp. Fe, Ce, Mn.

Test a small portion of this ppt. for Mn by boiling with HNO_3 and adding Pb_3O_4 : a purple supernatant solution=Mn.

Treat balance of ppt. by pouring boiling dil. H_2SO_4 over it; wash (In presence of H_3PO_4 turn to Phosphate Chart.)

Dpppp. Mn.

Dpppf. Fe, Ce.

Dissolve a few small crystals of $H_2\bar{O}$ by heat and cool.

Dpppfp. White crystalline ppt.=Ce.

Dpppff. Add $K_4Fe(CN)_6$: blue ppt.= Fe.

Test original solution for Fe(ous)with $K_6Fe_2(CN)_{12}$

For Fe(ic), with $K_4Fe(CN)_6$.

Dppf. Al, Cr.

(Yellow if Cr be present). Acidify with $H\bar{A}$, boil and divide into two parts. To one add Na_2HPO_4 and boil : white gelatinous ppt. =Al.

To other add a few drops $Pb\bar{A}_2$: an *immediate* yellow ppt.=Cr.

Dpf. Group III. Mn(?), Co, Ni, Zn.

Evaporate filtrate and washings to dryness, ignite to remove NH_4 salts; dissolve in hot dil. HCl, transfer to beaker, add NaOH in excess, then NaClO, *boil for a few minutes*, filter and wash.

Dpfp. Mn, Co, Ni.

Treat ppt. with $(NH_4)_2CO_3$ mixed with a few drops of alcohol.

Dpfpp. Mn, Co.

Test a small portion of ppt. for Mn according to **Dppp.**

Test a small portion for Co by Borax Bead test : Blue, hot or cold.

Dpfpf. Ni.

Blue or greenish solution. Add H_2S and test ppt. for Ni by Borax Bead test : Violet, hot; Brown, cold.

Dpff. Zn.

Add $Na_2S_2O_3$, boil and test for Zn by adding H_2S=white ppt.

Phosphate Chart.

Test **Dpp** for H_3PO_4 by dissolving a very small portion in HNO_3 adding $(NH_4)_2MoO_4$ in excess and warming : a yellow ppt.=H_3PO_4. Follow out directions of the regular chart until **Dpppp** and **Dpppf** are reached, then continue as follows :

<table>
<tr>
<td colspan="3">xDpppp. Mn(?), Ba, Sr.
Repeatedly pour warm $(NH_4)_2CO_3$ over ppt. and wash; throw away solution and washings. Treat ppt. with $H\bar{A}$ and wash.</td>
<td colspan="4">xDpppf. Fe, Ce. (Mn?), Ca, Mg.
Add Na_2HPO_4, then NaOH and NaClO, <i>boil for several minutes</i>, acidify with $H\bar{A}$, boil and filter.</td>
</tr>
<tr>
<td rowspan="2">xDppppp.
Mn(?) Ba.
Confirm by flame test: Green flame after heating and moistening with HCl.</td>
<td colspan="2">xDppppf.
Add K_2CrO_4.</td>
<td colspan="2">xDpppfp. Fe, Ce, Mn.
Treat with boiling dil. H_2SO_4, wash.</td>
<td colspan="2">xDpppff. Ca, Mg.
Add $(NH_4)_2C_2O_4$.</td>
</tr>
<tr>
<td>xDppppfp.
Yellow ppt. Ba. (Should be negative.)</td>
<td>xDppppff.
Add dil. H_2SO_4, allow to stand ten minutes; collect, wash and confirm Sr by flame test.</td>
<td>xDpppfpp.
Mn.</td>
<td>xDpppfpf.
Fe, Ce.
Test for Ce by adding $H_2\bar{O}$=white crystalline ppt.
Test for Fe in original solution.</td>
<td>xDpppffp.
Ca=white ppt.</td>
<td>xDpppfff. Mg.
Concentrate, cool, add NH_4OH and $(NH_4)_2HPO_4$, stir: white crystalline ppt.=Mg.</td>
</tr>
</table>

Direct Tests for Metals in Original Solutions

Are sometimes necessary or very desirable to avoid repetition of a tedious analysis :

Na, NH_4, Fe(ous) and **Fe(ic)** have been given on page 28.

Sn in old solutions may be filtered out in Group VII and lost. To 2 cubic centimeters of solution add 5 cubic centimeters HCl (1.12) and a bunch of card-teeth, warm to start the reaction and proceed as in **Cpfpfb.**

As : Start at **Bf,** collect precipitate, wash and treat with $(NH_4)_2CO_3$ as in **Cpfpp.**

Mn : Evaporate 2 or 3 drops twice with 2 cubic centimeters HNO_3 to remove HCl and interfering substances, dissolve in HNO_3, and add Pb_3O_4 as in **Dppp.**

Cr is frequently missed through insufficient boiling with NaClO ; to a little of the solution add NaOH and NaClO and proceed as in **Dpp** and **Dppf.**

Ba and **Sr:** Add an equal volume dil. H_2SO_4, let stand for ten minutes, collect on filter, wash with H_2O and treat the precipitate as given in **xDpppp** with $(NH_4)_2CO_3$. In this test **Ba, Sr** and **Pb** are precipitated as sulphates, the latter two are decomposed into carbonates by the $(NH_4)_2CO_3$, and later dissolve in Acetic Acid ; on adding K_2CrO_4 **Pb** is precipitated as yellow $PbCrO_4$ and the filtrate is tested for **Sr.** $BaSO_4$ is not decomposed by the above treatment and **Ba** is tested for as in **xDppppp.**

Hg. By acidifying solution with dil. HCl, adding a strip of Cu and allowing to stand ten minutes, the Hg will deposit on the Cu, causing a grayish stain, which by rubbing becomes silvery-white and lustrous ; remove from the liquid, rinse with H_2O and dry between filter paper. Drop the Cu into a piece of glass tubing, 100 to 150 millimeters long, closed at one end, and heat the Cu to vaporize the Hg ; soften and draw out that part of the tubing which contains the Cu, and leave a somewhat shorter tube, closed at one end, containing the Hg. Drop a minute fragment of I into this tube and heat until the I vapors are driven above the Hg sublimate, when there will usually be formed a scarlet, sometimes yellow becoming scarlet, sublimate of HgI_2.

As and **Sb. Marsh's Test :** A large test-tube (or a small flask) is adjusted with a cork carrying two tubes, one a funnel-tube reaching almost to the bottom of the test-tube, the other a short tube bent at an angle of 45° and drawn out into a rather fine point. Place some Zn in the tube, cover with a dilute $AgNO_3$ solution, let stand several minutes, and wash thoroughly with H_2O ; cover Zn with H_2O, adjust cork and pour some concentrated H_2SO_4 through the funnel-tube. After the air has been displaced by the evolved H, ignite the H escaping from the generator and allow the flame to strike upon a cold porcelain crucible lid ; if no dark stain is produced after several minutes, the reagents are free from condemning impurities, and a little of the solution to be tested is added through the funnel-tube and rinsed in with H_2SO_4. If **As** is present the flame will deposit a brown lustrous stain upon cold porcelain ; the gas passed through a piece of difficultly fusible glass-tubing drawn out at several places and heated near the narrow portions will give the same deposit in the tube. The gas passed into $AgNO_3$ gives a black precipitate of Ag, the **As** as H_3AsO_3 going into solution ; filter out the Ag and carefully neutralize with dilute NH_4OH, when yellow Ag_3AsO_3 will precipitate.
The **As** stain is readily soluble in NaClO and very slowly soluble in Na_2S.
The **Sb** stain, black and sooty, is insoluble in NaClO and readily soluble in Na_2S ; the precipitate formed with $AgNO_3$ has the composition Ag_3Sb, the Sb not going into solution.

Gutzeit's Test : H is generated in a test-tube, using Zn and dil. H_2SO_4; a plug of cotton is loosely pushed into the tube and the mouth of the test-tube covered with several thicknesses of filter paper, on the top one of which a drop of strong $AgNO_3$ solution is placed. If the $AgNO_3$ is not discolored after some time, showing the purity of the reagents, another test is made, but in which some of the solution to be tested is added. **As** causes a yellow stain which is turned black upon moistening with H_2O; **Sb** gives a black stain at once.

Fleitman's Test: Carried out as the preceding test but using Zn or Al and strong NaOH or KOH solution to generate the H. In presence of **As** a black stain is produced, while **Sb** does not respond in this test.

The preceding tests depend upon the reducing action of nascent H upon compounds of **As** and **Sb** forming gaseous H_3As and H_3Sb and the ready decomposition of these by heat and $AgNO_3$; or by chilling the flame of the burning gas only the H burns, depositing **As** or **Sb.**

Reinsch's Test: Depends upon the reduction of As and Sb compounds by Cu in presence of HCl, the **As** and **Sb** forming a black deposit on the Cu; if the Cu be heated in a piece of glass tubing closed at one end, **As** and **Sb** will oxidize forming sublimates of As_2O_3 and Sb_2O_3, the former of which is in octahedral crystals, the latter usually amorphous and much less volatile.

Bettendorff's Test: Depends upon the reducing action of a saturated HCl solution of $SnCl_2$ upon arsenical compounds with the separation of metallic **As** recognized by imparting a brown color, or by forming a brown precipitate.

If metallic Sn is added in making the test, as is sometimes directed, this will cause reaction also with Sb compounds.

Tests for Acids.

As in the Tests for Metals, there are many insoluble compounds that can be formed and used as Tests for Acids provided that only a single acid is present, precipitable by the reagent; but in mixtures of acids, so many of these insoluble compounds have a common solvent that the reagent is best employed under special conditions to positively detect a single acid.

To illustrate: The action of **$BaCl_2$**, as shown in the TABLE of TESTS for ACIDS, in neutral solution (absence of free acid) results in giving precipitates with all acids marked 1 and 2, and the non-formation of a precipitate would mean the absence of all of these acids; the formation of a precipitate in an unknown solution, however, could not be ascribed to any one acid, and other tests would finally have to reveal the particular acid. If the test be made as directed in the SCHEME for the DETECTION of ACIDS, H_2SO_4 is the only common acid which will respond.

$AgNO_3$ in the same way serves as the reagent for HCl (in Rule II, 3, *a*) disregarding other insoluble compounds that may be produced as AgBr, AgI, etc. and which are insoluble in dil. NH_4OH; under other conditions $AgNO_3$ is useful as a reagent for H_3PO_2, $H_2\overline{T}$, H_3AsO_3, H_3AsO_4, etc.

$CaCl_2$ is used as reagent for H_2CO_3, H_2SiO_3, $H_2\overline{O}$, $H_2\overline{T}$, $H_3\overline{C}$, etc.

Fe_2Cl_6 for acids given in Rule XII.

$HgCl_2$ for H_3PO_2 and other reducing acids.

$Pb\overline{A}_2$ for H_2S, H_2CrO_4 (in testing for metals), etc.

$CuSO_4$ for H_3AsO_3, H_3AsO_4, $H_4Fe(CN)_6$, etc.

Other important tests are given in the TABLE and refer to the tests used in the SCHEME for the DETECTION of ACIDS; this TABLE is supplemented by additional information in the TABLE of SOLUBILITY (page 15) and TABLE of TESTS for METALS (page 19).

Special Behavior of some Acids:

1. Those containing **As, Cr** and **Mn** will always be found in testing for Metals or Bases.
2. **Oxidizing** and **Reducing Acids** frequently destroy or alter each other; therefore, if added in proper proportions, neither can be found, but the products of alteration often enable one by inference to indicate the original substances; if added in other proportions, the one in excess will be found.

   The reactions for these decompositions are given in the section under **Oxidation** and **Reduction** (pages 9 to 12); some of these take place under all conditions, as

   NaClO with Na_2S, Na_2SO_3, KI, NaH_2PO_2, H_3AsO_3;

   in others again only in presence of free acid, as

   HI with HIO_3, HNO_2, H_2CrO_4, $H_2Mn_2O_8$, etc.
   HIO_3 with HI, H_2S, H_2SO_3, SO_2, etc.

Table of Tests for the Acids.

Use Salts of Alkali Metals in making these tests.	$AgNO_3$	$BaCl_2$	$CaCl_2$	$CuSO_4$	Fe_2Cl_6	$HgCl_2$	$Pb\bar{A}_2$	Tests made in the "Scheme for the Detection of Acids," and Special Tests for the Rarer Acids.
Acetic					1			I, 3; XI; XII; XIII; XIV.
Arsenic	1	1	1	1	1	1	1	X; $AgNO_3$; $CuSO_4$; $HCl + H_2S$.
Arsenous	1	1	1	1	1	1	1	X; $AgNO_3$; $CuSO_4$; $HCl + H_2S$.
Benzoic					1			II, 2; XI; XII; free acid sublimes.
Boric	1			1	1	1		I, 2; V, 3; VI; free acid sublimes.
Bromic								II, 1.
Bromine, free							2	I, 1; I, 3; V, 5; VIII.
Carbonic	1	1	1	1	1	1	1	I, 2; II, 1; XII; XIII.
Chloric								VI; VIII.
Chlorine, free							2	I, 3; V, 5; VIII.
Chromic	1	1		1	1	1	1	I, 1; V, 6; VIII; $NH_4OH + H_2S$.
Citric	1	1	1	1			1	XI; XIII.
Formic	2			1	1	2		XII; $AgNO_3$; $HgCl_2$.
Gallic	2			1	2	1	1	II, 2; XI; XII.
Hydrates, soluble	1		1	1	1	1	1	I, 2; XII; no acids will be found.
Hydriodic	2			1	1	1	2	II, 1; II, 3, b; XII.
Hydrobromic	2						1	II, 3, b.
Hydrochloric	2						1	II, 3, a.
Hydrocyanic	2			1				I, 2; I, 3; II, 1; III.
Hydroferricyanic	2			2	2			I, 1; II, 1; VIII; XI; XII.
Hydroferrocyanic	2			2	2	1	2	I, 1; II, 1; XI; XII.
Hydrofluoric		2	2					Concentrated H_2SO_4: etches glass.
Hydrosulphuric								See Sulphides.
Hydrosulphurous	1				1	2		VIII; $HgCl_2$.
Hypochlorous	2						1	I, 3; II, 1; V, 5; VIII.
Hypophosphorous	2			2	1	2		II, 3, a; II, 3, c; VIII; X; XI.
Iodine, free								I, 1; I, 3; V, 4; VIII.
Lactic								XI; XIII; Zn or Ca salt under microscope.
Malic	1						1	XI; XIII; free acid sublimes.
Nitric								VIII; IX.
Nitrous	1							II, 1; V, 6; VIII.
Oleic	2	2	2	2	2	2	2	I, 2; II, 2, liquid; XI.
Oxalic	1	1	1	1	1	1	1	XI; XIII; free acid sublimes.
Oxides, soluble	1		1	1	1	1	1	No acids will be found.
Palmitic	2	2	2	2	2	2	2	I, 2; II, 2, solid; XI.
Permanganic								I, 1; V, 6; VIII.
Metaphosphoric	1	1	1	1	1	1	1	X; $AgNO_3$; precipitates albumen.
Orthophosphoric	1	1	1	1	1	1	1	I, 2; X; XII; $AgNO_3$.
Pyrophosphoric	1	1	1	1	1	1	1	X; $AgNO_3$.
Salicylic				1	1	1	1	II, 2; XI; XII; free acid sublimes.
Silicic	2	2	2	2	2	2	2	I, 2; II, 2; X; XIII.
Stearic	2	2	2	2	2	2	2	I, 2; II, 2, solid; XI.
Succinic					1		1	XI; XII; XIII; free acid sublimes.
Sulphides	2			2	1	2	2	I, 2; I, 3; II, 1; V, 1; V, 2; VIII; XII.
Sulphocarbolic					1			XI; Fe_2Cl_6.
Sulphocyanic	2			2	1		1	XI; XII.
Sulphuric		2	1				2	VII.
Sulphurous	1	1			1	1	1	II, 1; IV.
Tannic	2			1	2	1	1	XI; XII.
Tartaric	1		1	1		1	1	XI; XIII.
Thiosulphuric	2			2	1	2	2	II, 1; II, 2; XI; XII.
Valerianic					1		1	I, 3; XI; Fe_2Cl_6.

Key: 1 = Forms a precipitate or colored solution in absence of free acid.
2 = Forms a precipitate insoluble in acid; use an acid compatible with the metal of the reagent.
Blank spaces = No visible change due to solubility.

Scheme for the Detection of Acids.

(WHEN ONLY THE ALKALI METALS ARE PRESENT.)

I. 1. Note COLOR of solution:

H_2CrO_4, yellow; $H_2Cr_2O_7$, orange; H_2MnO_4, green; $H_2Mn_2O_8$, purple; $H_4Fe(CN)_6$, yellow; $H_6Fe_2(CN)_{12}$, red by transmitted, greenish by reflected light; **Free Br**, yellow to brown; **Free I**, yellow to red-brown.

2. Note REACTION of solution:

a. If alkaline: Salts of the following acids are indicated:

(OH), H_2CO_3, H_2S, H_2SiO_3, H_3BO_3, H_3PO_4, HCN, $H\overline{Ol}$, $H\overline{Pal}$, $H\overline{St}$.

b. If acid: Free acid or salts having an acid reaction, see page 40.

c. If neutral: Salts having a neutral reaction.

3. Note ODOR of solution:

Free I: colors Starch-paper, moistened with H_2O, *blue*.

Free Cl or **Br**, colors KI and Starch-paper, moistened with H_2O, *blue*.

$HClO$, HCN, H_2S(?), $H\bar{A}$(?), $H\overline{Val}$.

If reaction be acid, also the following:

H_2S, H_2SO_3: vapors color KIO_3 and Starch-paper, moistened with H_2O, *blue*.

HNO_2: vapors color KI and Starch-paper, moistened with H_2O, *blue*.

II. ACTION OF DIL. H_2SO_4: may cause liberation of gases (effervescence) having color, odor and action upon moistened Test-papers, or cause formation of precipitates.

To 2 to 3 cubic centimeters of the original solution add an equal volume of dil. H_2SO_4 and note the effect before and after warming:

1. GASEOUS or VOLATILE BODIES evolved:

CO_2 from H_2CO_3; colorless, odorless; confirmed in **XIII**.

HCN from **cyanides**; evolved in the cold: colorless, odorous; confirmed in **III**.

HCN from $H_4Fe(CN)_6$ or $H_6Fe_2(CN)_{12}$; evolved above 60° C.; confirmed in **XII**.

H_2S; colorless, odorous; blackens $Pb\bar{A}_2$ paper, and turns KIO_3 and Starch-paper *blue*.

SO_2 from H_2SO_3 and $H_2S_2O_3$; colorless, odorous; turns KIO_3 and Starch-paper *blue*.

I; violet vapor, odorous; turns Starch-paper blue. **HI** in presence of dilute acids and $H_2Mn_2O_8$, H_2MnO_4, H_2CrO_4, $H_2Cr_2O_7$, $HClO$, HIO, HIO_3, HNO_2, (Fe(ic) and **Cu** salts) is decomposed, liberating **I**; this, depending upon the quantity, may remain in solution, causing a yellow or brown color, or may precipitate as a black powder.

Cl from $HClO$; yellowish-green, odorous; turns KI and Starch-paper *blue*.

Br from HBr, and $HBrO$ or $HBrO_3$; yellow, odorous; turns KI and Starch-paper *blue*.

N_2O_3 from HNO_2; red, odorous; turns KI and Starch-paper *blue*.

2. PRECIPITATE is produced:

S from $H_2S_2O_3$: fine white precipitate, difficult to retain on filter; if attended by odor of SO_2 (**II**, 1) = $H_2S_2O_3$.

H_2SiO_3: white, gelatinous precipitate; confirmed in **XIII**.

$H\overline{Benz}$, $H\overline{Sal}$, $H\overline{Gal}$: white, crystalline precipitates, soluble in hot H_2O; also in ether; confirmed in **XII**.

$H\overline{Ol}$, $H\overline{Pal}$, $H\overline{St}$: white, curdy precipitates, insoluble in hot H_2O, fusing to oily liquids; soluble in ether, chloroform, benzin, etc., etc.

I: black precipitate. See **II**, 1.

3. Boil until solution is free from odor of HCN, SO_2 and H_2S, particularly as these interfere with the following tests; prevent concentration of the solution by replacing the evaporated water; filter, if necessary, and divide into three parts:

a. To one part add a few drops HNO_3 and then $AgNO_3$, until no further precipitation takes place; collect upon a filter, wash with H_2O and throw filtrate and washings away. Treat precipitate on filter several times with NH_4OH (1 per cent., NH_3, which will not dissolve AgBr or AgI) and acidify the filtrate with HNO_3; a white, curdy precipitate = **HCl**.

In presence of H_3PO_2 or in a solution containing $H_2S_2O_3$ not thoroughly decomposed by sufficient boiling, a black precipitate may be produced upon adding $AgNO_3$, but this will not interfere with the HCl test as given above.

b. To another portion add a few drops of starch solution and then carefully add chlorine water; blue color = **HI.** (In presence of acids, which can liberate I from HI (see above **II**, 1), the HI may be entirely decomposed, and no test will be obtained at this stage. A colorless original solution, liberating I on acidifying with diluted H_2SO_4 = **HI.**)

Continue the addition of chlorine water until the solution smells of Cl after agitation; then add a few drops $CHCl_3$ and agitate; yellow color in $CHCl_3$ = **HBr.** The excess of Cl combines with the I to form a colorless compound, while the Br liberated by the Cl does not yield a colorless compound unless a very large excess of chlorine water be added. If the $CHCl_3$ separates with a pink or violet color, I is still present, and more chlorine water must be added.

c. To the third portion add HCl and $HgCl_2$ and warm; a white, silky precipitate = **H_3PO_2.** In presence of HI a red precipitate may form upon addition of $HgCl_2$, but this will dissolve upon adding more $HgCl_2$, and upon boiling a yellow precipitate (Hg_2I_2) may form = **H_3PO_2.**

In presence of $H_2S_2O_3$, not thoroughly decomposed by boiling with the diluted H_2SO_4, a white turbidity may be produced, but this differs so in appearance from the H_3PO_2 test that it should not be mistaken.

III. To 1 cubic centimeter of the original solution, add one or two drops $FeSO_4$, followed by a few drops Fe_2Cl_6, then make alkaline with NaOH, warm and acidify with HCl: blue color or precipitate = **HCN**; if too much of the iron salts be added a green solution may result (a combination of blue and yellow colors), which is equally characteristic, and which, after standing, will deposit the blue precipitate. PRUSSIAN BLUE TEST.

IV. Make 2 cubic centimeters of the original solution faintly alkaline with Na_2CO_3, if necessary; then add 5 cubic centimeters $ZnSO_4$, one piece of Nitro-prusside-paper and two drops $K_4Fe(CN)_6$: a pink or rose-colored mixture = **H_2SO_3.**

V. BEHAVIOR of ACIDS and SALTS towards TEST-PAPERS. Dip a clean glass rod into the original solution and with the adhering drop moisten one end of a piece of the respective test-paper.

1. $Pb\bar{A}_2$ paper: turns brown or black with **H_2S** or soluble sulphides.
2. Nitro-prusside-paper: turns purple with soluble sulphides = **H_2S.**
3. Mix a few drops of the original solution with an equal volume of diluted HCl; with this mixture moisten a piece of Turmeric-paper and allow to *dry perfectly*: a red-brown color which, upon an addition of one drop of NH_4OH, turns blue-black = **H_3BO_3.**
4. Starch-paper: turns blue with **free I.**
5. If **V**, 4, does not respond, try KI and Starch-paper: turns blue with **free Cl, free Br, HClO.**
6. If **V**, 5, does not respond, moisten the same piece of paper with $H\bar{A}$: turns blue = **HNO_2, H_2CrO_4, $H_2Cr_2O_7$, H_2MnO_4, $H_2Mn_2O_8$.**

VI. ACTION of CONCENTRATED H_2SO_4. This causes the liberation of such a number of gaseous products that in mixtures of acids but little satisfaction follows its use, owing to reactions between some of the gaseous products, or to the decomposition of the H_2SO_4 by them.

Neutralize 1 cubic centimeter of the original solution with NaOH, if necessary; evaporate to dryness, cool, add a few drops of concentrated H_2SO_4, stir, add a small quantity of alcohol, stir and ignite the alcohol: a green flame = **H_3BO_3.** Cu and Ba salts, with volatile acids like HCl, etc., etc., may also impart a green color to burning alcohol, but this is not the case with the sulphates.

In the absence of HI, or HBr and HNO_3, the addition of the H_2SO_4 may be used to indicate the presence of **$HClO_3$** by the liberation of greenish-yellow Cl_2O_4.

VII. 1. Mix equal volumes of dilute HCl and $BaCl_2$, filter, if necessary, and divide into two parts; to one add 2 cubic centimeters of the clear original solution, to the other add 2 cubic centimeters of distilled water: an increased turbidity or precipitate in the former as compared with the latter = **H_2SO_4**.

2. If a precipitate was produced in **II**, 2, the same precipitate will form when dilute HCl is used in **VII**, 1, and of course interfere with the test for H_2SO_4. In such cases, proceed as follows:

Take 2 cubic centimeters of the original solution in one test-tube, a like quantity of distilled H_2O in another, then add the same quantity of dilute HCl to each, boil and filter; to the clear filtrates now add $BaCl_2$ and compare tests as above.

VIII. ACTION of SALTS and ACIDS upon INDIGO-PAPER.

The discharge of the blue color (decoloration) may be due to an oxidizing action producing *Isatin:* Cl, Br, I, $HClO$, $HClO_3$, HNO_2, HNO_3, $H_6Fe_2(CN)_{12}$, H_2CrO_4, $H_2Cr_2O_7$, $H_2Mn_2O_8$, H_2MnO_4; or to a reducing action producing *Indigo-white:* H_2S, H_2SO_2, H_3PO_2.

To determine if decolorization is taking place, carry through a blank test in which H_2O is used instead of the original solution, adding all reagents in like quantities.

1. Make 3 cubic centimeters of the original solution slightly alkaline with Na_2CO_3 (if alkaline omit the Na_2CO_3) and add a piece of Indigo-paper: decolorization = **free Cl, free Br, free I, $HClO$, H_2S, H_2SO_2, $H_6Fe_2(CN)_{12}$, H_2MnO_4, $H_2Mn_2O_8$.** With **free I**, it is necessary to remove the paper, wash with H_2O and decolorize the blue color which the latter may give the paper by adding a few drops $Na_2S_2O_3$.

2. If **VIII**, 1, is not decolorized, remove the test-paper, acidify the solution with dilute H_2SO_4 and allow to stand for several minutes: decolorization = **HNO_2, H_2CrO_4, $H_2Cr_2O_7$.**

If a precipitate of I results in **II**, 2, the same precipitate will form in **VIII**, 2, and interfere with the recognition of the decolorization; in this case filter and notice decolorization in the filtrate.

3. If **VIII**, 2, is not decolorized, add a few drops of $Na_2S_2O_3$ and allow to stand ten minutes without heating: decolorization = **$HClO_3$, H_3PO_2.**

In solutions containing H_2SO_3 or $H_2S_2O_3$, **$HClO_3$** and **H_3PO_2** will bring about decolorization in **VIII**, 2, and this may be attributed to **HNO_2**. As stated $HClO_3$ brings about decolorization by oxidation, which is a permanent change; H_3PO_2 by reduction, a temporary change; in the latter case by allowing the test to stand, exposed to the air, the Indigo-white will absorb O and change again to Indigo-blue.

4. If **VIII**, 3, is not decolorized, add an equal volume of concentrated H_2SO_4: decolorization = **HNO_3**.

5. If **VIII**, 1 or 2, is decolorized, add 3 cubic centimeters $H\bar{A}$ to 5 cubic centimeters of the original solution, evaporate to dryness, add 3 cubic centimeters $H\bar{A}$ and again evaporate to dryness; dissolve in 5 cubic centimeters H_2O and divide into two parts; to one add dilute H_2SO_4 and a piece of Indigo-paper and repeat tests **VIII**, 3 and 4; test the other portion according to **IX**, if HNO_2 is indicated by **II**, **V** and **VIII**.

IX. To 3 cubic centimeters of the original solution, if HNO_2 be absent, or of **VIII**, 5, if HNO_2 be present, add an equal volume of concentrated H_2SO_4 (if a dark color or precipitate of I from HI results, agitate and cool to cause the separation of the I and the formation of a comparatively light-colored solution, which will not interfere with the test), and then add a solution of $FeSO_4$ in dilute H_2SO_4 so that this will form a distinct layer upon the heavier concentrated H_2SO_4 solution: a brown ring at the juncture of the two liquids due to solution of N_2O_2 in the excess of $FeSO_4$ = **HNO_3**.

In presence of $HClO_3$, which is a stronger oxidizing agent than HNO_3, this test may fail because the $HClO_3$ oxidizes the ferrous salt to ferric salt and prevents the action of the HNO_3. In case $HClO_3$ is found in **VI** or **VIII**, make 3 cubic centimeters of the original solution alkaline with $NaOH$, add a crystal of $FeSO_4$, boil until the green $Fe(OH)_2$ is oxidized by the $HClO_3$ to brown $Fe_2(OH)_6$ (HNO_3 will not do this in alkaline solution), filter and in the filtrate make the test for HNO_3 according to **IX**.

X. BEHAVIOR of ACIDS towards AMMONIUM MOLYBDATE. This is primarily the test for **H_3PO_4**, but will also respond under slightly different conditions of temperature with **H_2SiO_3** and **H_3AsO_4**; the conditions for removing interfering acids like HCl, H_2SO_3 and $H_2S_2O_3$ by evaporation with HNO_3 will change **H_3PO_2** and **H_3AsO_3** into H_3PO_4 and H_3AsO_4, respectively, and complicate matters. The alternate test for **H_3PO_4** by use of Magnesia Mixture is also responded to by **H_3AsO_4**, but not by **H_3PO_2**.

From this it will be seen that to obtain a conclusive test for H_3PO_4 the presence or absence of the above-mentioned acids must be established by prior tests.

a. **H_2SiO_3** must be removed by evaporation to dryness with HCl or HNO_3, redissolving in HCl or HNO_3 and filtering out the white gelatinous H_2SiO_3.

b. **H_3AsO_3** and **H_3AsO_4** must be removed by acidifying with HCl and precipitating with H_2S and filtering.

1. If H_3PO_2 (**II**, 3, **c**; **VIII**, 3), H_3AsO_3 and H_3AsO_4 (found in Group V in testing for metals) are absent, add HNO_3 to a *few drops* of the original solution, evaporate to dryness, redissolve in HNO_3, filter to remove H_2SiO_3, add an excess, 5 cubic centimeters, $(NH_4)_2 MoO_4$ to filtrate and warm: a yellow precipitate = **H_3PO_4**.
2. If H_3PO_2 is absent, but H_3AsO_3 or H_3AsO_4 is present, add dilute HCl and H_2S to precipitate As; filter, add HNO_3 to filtrate, evaporate to dryness and proceed as in **X**, 1.
3. If H_3PO_2 is present, but H_3AsO_3, H_3AsO_4 and H_2SiO_3 absent, add NH_4OH in excess to 3 cubic centimeters of the original solution and then 5 cubic centimeters of Magnesia Mixture and stir: white crystalline precipitate = **H_3PO_4**.
4. If H_3PO_2 and H_3AsO_3 or H_3AsO_4 are present, precipitate As by adding dilute HCl and H_2S and filter; boil filtrate to expel H_2S and filter; cool, add NH_4OH in excess, then Magnesia Mixture and stir: white crystalline precipitate = **H_3PO_4**.
5. A small portion of the precipitate obtained in **X**, 3 or 4, after washing, dissolved in HNO_3 and warmed with an excess of $(NH_4)_2 MoO_4$, should give a yellow precipitate = **H_3PO_4**. The precipitate obtained with $(NH_4)_2 MoO_4$ has the composition $(NH_4)_3 PO_4\ 12MoO_3$, from which it will be seen that a large quantity of $(NH_4)_2 MoO_4$ must be employed in the test.

XI. HEAT or CHAR TEST. Evaporate 1 cubic centimeter of the original solution to dryness on a crucible lid and heat: a black residue (in absence of salts of Fe, Mn, Ni, Co and Cu, which yield black oxides) = **C** from **Organic Acids.** Nitrates, chlorates, hypochlorites, etc., by giving up oxygen during the heating interfere more or less with this test.

If the residue does not char only **$H\bar{A}$** and **$H_2\bar{O}$** of the organic acids need be tested for. **H_3PO_2** and **$H_2S_2O_3$** may be indicated in this test by catching on fire and by the odor emitted (H_3P and SO_2, respectively.)

XII. To 3 cubic centimeters of the original solution (which, if acid, should be made faintly alkaline with NH_4OH, boiled to remove excess of NH_4OH and cooled), add Fe_2Cl_6:

1. A red color:

   (OH), H_2CO_3, $H\bar{A}$, $H\bar{F}$, HCNS, HI; the first four are decolorized by HCl forming a yellow solution; the fifth by HCl and $HgCl_2$; the sixth may separate crystals of **I** and will yield its color to $CHCl_3$.
2. A violet color:

   $H_2S_2O_3$, color speedily disappears.

   $H\overline{Sal}$, color permanent; confirm by mixing small quantities of methyl alcohol and concentrated H_2SO_4, adding a little of the original solution, boiling, cooling and noting odor of methyl salicylate (oil of wintergreen.)
3. A black or blue-black color (or precipitate):

   $H\overline{Gal}$, $H\overline{Tan}$; the latter is distinguished from the former in the original solution by giving a precipitate with gelatin solution.

   H_2S, in larger quantities, may give a black precipitate of FeS.
4. A brown (or olive) color:

   $H_6Fe_2(CN)_{12}$; confirm in original solution with $FeSO_4 + HCl$: dark-blue precipitate.

5. A white precipitate :

H_3PO_4; S from small quantities of H_2S.

6. A pink precipitate :

$H\overline{Benz}$; soluble in warm HCl, depositing crystals of $H\overline{Benz}$ upon cooling.

7. A brown precipitate :

(OH), H_2CO_3; after boiling : $H\bar{A}$, $H\bar{F}$, $H_2\overline{Suc}$.

8. A dark-blue precipitate :

$H_4Fe(CN)_6$; insoluble in HCl.

XIII. To 3 cubic centimeters of the original solution (which, if acid, is made faintly alkaline with NH_4OH, the excess of NH_4OH boiled off and the solution cooled), add $CaCl_2$ in excess, to insure complete precipitation, stir* vigorously for several minutes, collect precipitate upon filter and wash with cold H_2O.

<table>
<tr><td colspan="4">Ppt. H_2CO_3, H_2SiO_3, H_3BO_3, H_3PO_4, $H_2\bar{O}$, $H_2\bar{T}$, etc., etc.
Wash thoroughly with cold H_2O until washings no longer react for HCl with $AgNO_3$ (throw away washings); treat ppt. on filter with boiling H_2O.</td><td colspan="2">Filtrate $H_3\bar{C}$, $H\bar{A}$, HCl, HNO_3, H_2SO_4, etc., etc.
Evaporate almost to dryness, add NH_4Cl, evaporate (note odor of $H\bar{A}$ as solution approaches dryness); again add NH_4Cl (and NH_4OH, if solution is acid) and boil.†</td></tr>
<tr><td colspan="3">Ppt. H_2CO_3, H_2SiO_3, H_3BO_3, H_3PO_4, $H_2\bar{O}$.
Treat with boiling dilute H_2SO_4 and watch for effervescence = H_2CO_3.</td><td rowspan="3">Filtrate $H_2\bar{T}$, cool and add to a small portion of the filtrate 1 cubic centimeter $AgNO_3$ (if a ppt. forms the washing with cold H_2O was incomplete and a silver-mirror is not likely to be obtained) and one drop NH_4OH and carefully heat:
Silver-mirror or black ppt. = $H_2\bar{T}$.</td><td rowspan="3">Ppt. $H_3\bar{C}$: white crystalline.</td><td rowspan="3">Filtrate $H\bar{A}$, HCl, HNO_3, H_2SO_4, etc., etc.
Malic and **Succinic** acids, if present, will be found in this filtrate and can be precipitated by adding alcohol.</td></tr>
<tr><td rowspan="2">Ppt. H_2SiO_3 (H_2SO_4). Wash thoroughly with cold H_2O to remove H_2SO_4; white gelatinous ppt. = H_2SiO_3.</td><td colspan="2">Filtrate H_3BO_3, H_3PO_4, $H_2\bar{O}$. Add NH_4OH in excess, then $H\bar{A}$ in excess.</td></tr>
<tr><td>Ppt. $H_2\bar{O}$: fine white crystalline.</td><td>Filtrate H_3BO_3, H_3PO_4. (disregard.)</td></tr>
</table>

XIV. 1. Mix 3 cubic centimeters each of alcohol and concentrated H_2SO_4 and divide into two parts; to one add 2 cubic centimeters of the original solution; to the other the same quantity of distilled H_2O; boil both, allow to cool and compare odors: odor of acetic ether = $H\bar{A}$.

2. The formation of ammonium acetate, by mixing equal volumes of original solution and NH_4Cl, and the decomposition of this, when evaporated almost to dryness, with evolution of vapors of acetic acid, is a better test than **XIV**, 1, because there is but one odor evolved.

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* By stirring with a glass rod, crystalline Calcium Tartrate generally separates, at least in part, on the sides of the test-tube; when this is the case the mixture can be filtered, the test-tube rinsed quickly with three or four small portions of H_2O to thoroughly remove chlorides and the test for $H_2\bar{T}$ made with the slight precipitate still adhering to the test-tube by adding 3 to 5 cubic centimeters H_2O, 1 cubic centimeter $AgNO_3$ and 1 drop NH_4OH (5 per cent.) and gently heating for several minutes. If the test is successful, it is not necessary to wash the main precipitate so thoroughly as to remove all chlorides, which will save much time; if the test is not successful, the directions in the chart must be carefully followed.

† This test depends upon the formation of Calcium Citrate, which is less soluble in hot than in cold solutions; it may be necessary to evaporate the solution in NH_4Cl two or three times before the Calcium Citrate assumes the crystalline form which is insoluble in NH_4Cl.

Notes on Testing for Bases and Acids.

Never test for an Acid or Base which has been added in the course of the analysis.

Solutions.

Bases. Read the explanatory statements on the action of certain acids in testing for bases, as given on pages 21, 24 and 35.

Acids. The detection of the bases will give a clue to the acids likely to be present, especially if the reaction of the solution is considered in connection with the Table of Solubilities and Table of Tests for Metals, pages 15 and 19; salts of **Al, Au, Bi, Cu, Fe, Hg, Mn, Pb, Sb,** etc., soluble in H_2O, give an acid reaction. Remember that acids of **As, Cr** and **Mn** will always be found among the bases, although **Cr** and **Mn** may also be present as bases.

A. If the solution gives no precipitate, or evolves no NH_3, with Na_2CO_3, added to strong alkaline reaction and boiled, proceed according to the Scheme for the Detection of Acids; remember, however, that color in the solution may be due to Bases under certain conditions:

Blue: **Cu** or **Ni,** in presence of excess of NH_4OH, or of organic acids (like tartaric and citric), and alkaline hydrates or carbonates.

Green or *Violet:* **Cr** in presence of organic acids and alkali.

Red-brown: **Fe** in presence of organic acids and alkali (tests for **Fe** with $K_4Fe(CN)_6$ and $K_6Fe_2(CN)_{12}$ will not respond in this case unless sufficient HCl be added to combine with the alkali and liberate the organic acid).

B. If the solution gives a precipitate, or evolves NH_3 with Na_2CO_3 added to strong alkaline reaction, boil for ten minutes, filter and wash precipitate (disregard this precipitate which consists of the carbonates, hydrates or oxides of the metals); proceed as follows with the filtrate and washings:

a. With small portions apply **Rules I,** 1 and 3, **VI** and **XI.**

b. Acidify a portion with dil. H_2SO_4 and apply **Rules II, IX** and **XIV,** 1.

c. Acidify a few drops with HNO_3 and apply **Rule X,** 1.

d. Neutralize a portion (or leave *faintly alkaline*) with dilute HCl and apply **Rules III, IV, V, VII, VIII, X,** 3, **XII, XIII and XIV,** 2.

Simple Solids.

The analysis of these is facilitated by a knowledge of the physical properties of the various chemical substances, as, for instance, *color, odor, physical structure, behavior upon heating* and the *solubilities,* particularly in H_2O and in dilute HCl.

I. Color: may change by exposure to laboratory fumes (reaction with H_2S).

II. Odor: for odors due to acids, see page 35; bases, excepting NH_4 in a few compounds like the carbonate, sulphide, etc., fail to produce odors.

III. Physical structure: may be well crystallized, crystalline or amorphous.

IV. Behavior upon heating on porcelain:

a. NO APPARENT CHANGE: $CaCO_3$, $Ca_3(PO_4)_2$, MgO, $NaHCO_3$, etc.

b. MELT IN THE WATER OF CRYSTALLIZATION, yielding a dry powder or mass after the H_2O is driven off: $Al_2K_2(SO_4)_4\ 24H_2O$, $Na_2HPO_4\ 12H_2O$, $Na_2CO_3\ 12H_2O$; etc., etc., in other cases the dry salt is decomposed with change of color:

$ZnSO_4\ 7H_2O$, $Na\bar{A}\ 3H_2O$, $Na_2S_2O_3\ 5H_2O$, etc., etc.

c. MELT READILY TO A CLEAR LIQUID, difficult to see while hot:

KNO_3, $KClO_3$, KI, $NaNO_3$, $KHSO_4$, $Na_2B_4O_7$, etc.

d. CHANGE IN COLOR, not due to carbonizing: Metallic salts, see E page 17.

e. BLACKENS, DUE TO CARBONIZING (separation of C): **Organic Acids**:

1. *Uncombined:* black residue of C gradually burning off; after cooling and moistening with H_2O, solution gives neutral reaction (if acid was thoroughly decomposed) and no flame test.
2. *Combined with* K, Na, Li: residue remains black after prolonged heating; after cooling and moistening with H_2O, solution gives an alkaline reaction (due to formation of carbonates) and flame test for the metal.
3. *Combined with heavy metals*, like Pb, Bi, etc.: residue speedily loses its black color and leaves a characteristic colored residue of oxide, see E page 17.

f. VOLATILIZES, leaving no residue: I, S, C, As_2O_3, As_2S_3, AsI_3, salts of Hg and NH_4 with volatile acids, and some uncombined organic acids which are volatile without decomposition (separation of C), as $H\overline{Benz}$, $H\overline{Sal}$, $H_2\overline{O}$, $H_2\overline{Suc}$, $H_2\overline{Mal}$.

V. Solubility in H_2O: Try cold H_2O first, if insoluble apply heat. If soluble, note reaction of solution and test portions for BASES and ACIDS. If the test for the acid is to be made in alkaline or acid solution and the base found will cause a precipitate with the necessary alkali or acid which interferes with the test, the powder or its aqueous solution should be boiled with an excess of Na_2CO_3 as directed under B page 40.

VI. If insoluble in H_2O, add sufficient **HCl** (1.12) to make the liquid equal in strength to dilute HCl; the addition of the HCl will frequently indicate the acid by an effervescence, odor or formation of a precipitate.

If soluble in **dilute HCl**, examine a portion of the solution for BASES; the base found and the preliminary tests in **IV** and reference to the Table of Solubilities should indicate the acid or acids likely to be present. A study of the tabulated examples will impress upon the student that much time can be saved by taking advantage of the preliminary tests and avoid making unnecessary tests; see page 42.

The following are among the more important compounds insoluble in dilute HCl: Salts of Ag, Hg(ous) and Pb(?), HgI_2, Sulphides of Groups V and VI, NiS, CoS, $BaSO_4$, $SrSO_4$, $CaSO_4$(?), Sb_2O_3, SnO_2, Fe_2O_3, Cr_2O_3, Al_2O_3, MnO_2, CaF_2, SiO_2, Silicates, S, C; Ferrocyanides, Ferricyanides and Chromates of the heavy metals, see Table, page 15.

VII. A simple test can be applied for many of the above by suspending some of the solid in H_2O, adding **dilute HCl** and then **H_2S**; if the solid in question is not a sulphide and belongs to Groups V-VII, it will change into a characteristic colored sulphide, see page 20.

VIII. Hot, concentrated HCl will dissolve CoS, NiS and Sulphides of Groups V and VI, excepting those of As, Au, Hg(ic) and Pt; MnO_2 and insoluble Chromates will be dissolved or decomposed, liberating Cl; Sb_2O_3, SnO_2 Fe_2O_3, Al_2O_3, Cr_2O_3 are but slightly soluble, especially if they had been ignited.

IX. HNO_3 and **Aqua Regiæ** can only be used for dissolving solids, if allowance is made for their oxidizing action: Hg(ous) salts are changed to Hg(ic), Fe(ous) to Fe(ic); Sulphides Sulphites, and Thiosulphates to Sulphates, As_2S_3 to H_3AsO_4 and H_2SO_4, Hypophosphites to Phosphates; Iodides and Bromides are decomposed, liberating I and Br. The sulphides of As, Au, Hg(ic) and Pt are dissolved by the last reagent.

X. Boiling with an excess of **Na_2CO_3 solution** for ten minutes will serve to decompose many insoluble compounds by abstracting the acid radical to form a soluble sodium compound, leaving an insoluble carbonate, hydrate or oxide of the metal. The mixture is filtered and the filtrate and washings tested for the acids; the insoluble part is dissolved in dilute HCl and tested for the base. As_2S_3 and precipitated SiO_2 will dissolve in the Na_2CO_3 solution, and can be reprecipitated by adding HCl, (the SiO_2 only perfectly after evaporating to dryness and adding HCl and H_2O). $PbSO_4$, $SrSO_4$ and $CaSO_4$ are easily decomposed by this treatment. Hg_2Cl_2 is decomposed, giving a black precipitate. $Ca_3(PO_4)_2$ is not decomposed by boiling with Na_2CO_3 solution.

Behavior of Typical Simple Solids in IV, V and VI.

	IV.				V.		VI.				Tests for Bases.			Acid or acids likely to be present, conforming to these tests and to the solubilities:
	Action of Heat.	Color of Residue.	Reaction of Residue.	Flame-test of Residue.	Sol. in H_2O.	Reaction of Solution.	Sol. in Dil. HCl.	Effervescence.	Precipitate.	Odor.	Ppt. in Group.	Color of Precipitate.	Base Found.	Roman numerals in this column refer to Rules for Acids, pages 35-39.
$H_2\overline{T}$	chars	none	neut.	none	yes	acid	yes	no	no	none	no	—	none	Free organic ; XII, XIII.
$KNa\overline{T}$	"	black	alk.	K,Na	"	neut.	"	"	"	"	"	—	K,Na	Organic ; XII, XIII ; ($H_2\overline{T}$.)
$KH\overline{T}$	"	"	"	K	"	acid	"	"	"	"	"	—	K	" XII, XIII ; ($H_2\overline{T}$.)
$K(SbO)\overline{T}$	"	"	"	K	"	"	"	"	?	"	V	red	K,Sb	" XII, XIII ; ($H_2\overline{T}$.)
$Pb\overline{A}_2$	"	reddish	neut.	none	"	"	?	"	?	$H\overline{A}$	VI	black	Pb	" XIV ; ($H\overline{A}$.)
$Pb(NO_3)_2$	color	"	"	"	"	"	?	"	?	none	VI	"	Pb	Inorganic ; $HClO_3$, $HBrO_3$ (HNO_3).
Na_2CO_3	no	white	str.alk.	Na	"	str.alk.	yes	yes	no	"	no	—	Na	" H_2CO_3.
$NaHCO_3$	no	"	"	Na	"	f. alk.	"	"	"	"	"	—	Na	" H_2CO_3.
$(BiO)_2CO_3$	color	yellow	neut.	none	no	—	"	"	"	"	VI	brown	Bi	" H_2CO_3.
$BiONO_3$	"	"	"	"	"	—	"	no	"	"	VI	"	Bi	" HCl, HNO_3, etc., etc.
$Na_2S_2O_3$	black	black	alk.	Na	yes	neut.	"	"	S	SO_2	VII	S	Na	XII ; ($H_2S_2O_3$.)
$Na\overline{Sal}$	chars	"	"	Na	"	"	"	"	$H\overline{Sal}$	no	VII	white	Na	Organic ; XII.
$H\overline{Sal}$	vol.	none	neut.	none	"	acid	"	"	no	"	no	—	none	Free organic ; XII.
$HgCl_2$	"	"	"	"	"	"	"	"	"	"	V	black	Hg	Inorganic ; HCl.
$HgNH_2Cl$	"	"	"	"	no	—	"	"	"	"	V	"	Hg	" HCl. (NH_4.)
Hg_2Cl_2	"	"	"	"	"	—	no	"	—	"	—	—	—	" See pages 41 and 43.
As_2O_3	"	"	"	"	"	—	yes	"	no	"	V	yellow	As	As_2O_3.
$KClO_3$	melts	white	"	K	yes	neut.	"	"	"	"	no	—	K	Inorganic } $HClO_3$, HNO_3,
KI	"	"	"	K	"	"	"	"	"	"	"	—	K	exc. I, 2 } HCl, HI, HBr.
$Na_2B_4O_7$	"	"	alk.	Na	"	alk.	"	"	"	"	"	—	Na	I, 2: H_3BO_3, H_3PO_4.
$Ca_3(PO_4)_2$	no	"	neut.	none	no	—	"	"	"	"	IV	white	Ca	Inorganic ; H_3PO_4.
$ZnSO_4$	melts	" (?)	acid	"	yes	acid	"	"	"	"	III	"	Zn	" H_2SO_4, HCl.
$Al_2K_2(SO_4)_4$	"	white	"	K	"	"	"	"	"	"	IV	"	K,Al	" H_2SO_4.
$MgSO_4$	"	"	neut.	none	"	neut.	"	"	"	"	II	"	Mg	" H_2SO_4.
$K_4Fe(CN)_6$	black	black	alk.	K	"	"	"	"	"	HCN	no	—	K	Organic ; XII.
Fe	no ?	"	neut.	none	no	—	"	yes	"	?	IV	black	Fe	CO_2 ; H_2S ; H.
H_3BO_3	melts	white	acid	green	yes	acid	"	no	"	no	no	—	none	Inorganic ; H_3BO_3.

XI. In special cases, as in the decomposition of insoluble Ferricyanides and Ferrocyanides, boiling with **NaOH** solution is more effective; test solution for acids, the precipitate for metals after washing and dissolving in HCl.

XII. In some cases the only treatment which succeeds in decomposing an insoluble compound is to mix it with three to four times its bulk of **dry** Na_2CO_3 and fuse on the platinum foil; after cooling, treat with H_2O: Cr_2O_3, Al_2O_3, SiO_2 will dissolve, due to formation of sodium salts as chromate (yellow color), aluminate and silicate, respectively; by acidifying with HCl, evaporating, adding HCl and H_2O a precipitate of SiO_2 will be obtained; by acidifying with HCl and examining for Bases, Al and Cr will be found.

Silicates are decomposed but do not become soluble in H_2O; decompose fused mass with HCl, evaporate to dryness, moisten with HCl, add H_2O, warm and filter; precipitate = H_2SiO_3, filtrate contains metals, which are tested for as usual.

$BaSO_4$ yields $BaCO_3$ and Na_2SO_4; the latter soluble in H_2O, the former insoluble in H_2O but soluble (after washing) in dilute HCl.

Mixed Solids.

To determine the exact composition of a mixture of solids it is best to effect a separation o the solids by the use of solvents; for this purpose use in succession H_2O (**V**), dilute HCl (**VI**) and as many of the other solvents or treatments (**VII–XII**) as may be necessary.

After the use of a solvent, wash the insoluble part thoroughly with H_2O allowing the washings to run into the solution. To determine if some of the solids have gone into solution in **V**, **VI**, **VIII** and **IX**, evaporate a small portion carefully to dryness on porcelain and note if a residue is obtained, this can then be further heated and behavior in **IV** noticed ; only in case a residue is obtained is it necessary to examine for bases and acids.

In **X**, **XI** and **XII** where a solid in solution is used as the solvent or decomposing agent, a residue of the reagent will always be obtained.

The solutions obtained in the separation are to be tested as stated under the respective treatment.

Alloys.

1. The usual method consists in *completely oxidizing* the metals constituting the alloy by heating with HNO_3 (1·20), evaporating to dryness, moistening the residue with HNO_3, adding hot H_2O, filtering and washing ; filtrate and washings are tested for metals according to the Chart.

   The portion insoluble in HNO_3 (SnO_2, Sb_2O_3, Au, Pt and, in presence of Au and Pt in larger quantities, Ag) is suspended in H_2O, acidulated with dilute HCl and saturated with H_2S; examine the precipitate for Groups V–VI and disregard the filtrate. If Ag be present in the portion insoluble in HNO_3, it will be found in **Cpfppp** in the part insoluble in dilute HCl, by treatment with NH_4OH and acidifying the filtrate with HNO_3.

2. Some Alloys containing Fe, Mn and Al are best dissolved by using **Aqua Regiæ**, evaporating to small bulk (or to dryness in case SiO_2 is to be sought for), adding dil. HCl and H_2O.

   This treatment will also be necessary if S and P are to be tested for, the filtrate giving tests for H_2SO_4 and H_3PO_4, respectively.

Qualitative Urinalysis.

NORMAL URINE is a complex excretion containing:

Inorganic Constituents: K, Na, (NH_4), Ca and Mg as chlorides, phosphates and sulphates; the Phosphates of the *alkali-metals* are soluble in water under all conditions, those of the *alkali-earth metals* are only soluble in acid solutions, and are precipitated upon the addition of alkalies; the Sulphates are present as *simple sulphates*, precipitable by $BaCl_2$, and as *ethereal-* or *conjugated-sulphates* (in which one H of H_2SO_4 is replaced by an organic (phenol) radical and the other H by a metal) not precipitable by $BaCl_2$ until after boiling with HCl which decomposes the ethereal-sulphates with production of simple sulphates.

Organic Constituents: Urea, Creatinine, Uric Acid, Hippuric Acid, Pigments, etc., and minute traces of Oxalic Acid, Acetone, Sugar, etc.

ABNORMAL URINE may contain inorganic or organic constituents in either largely diminished or largely increased quantities or may contain certain organic compounds which are the products of disease, as Sugar (Glucose or Dextrose), Acetone, Albumin, Peptone, Biliary Pigments, Blood, Pus, etc.

Volume. Normally 1,400 to 1,500 cubic centimeters in twenty-four hours; increased in diabetes, convulsions, cirrhosis of the kidneys, etc.; decreased at times to complete suppression, in acute fevers, inflammations, etc.

Color. Normally pale-yellow or amber. Diabetic urine is usually paler, due to greater volume and, hence, greater dilution of the normal pigments. Dark urines owe their color to excess of normal pigments, to bile-pigments, to blood or to the use of drugs: *Yellow*, turning *red* with alkalies, Senna, Rhubarb, Frangula, Santonin; *yellowish-red* to *blood-red*, Antipyrine, Sulphonal, Trional; *brown* to *black*, Phenol, Cresol, Resorcin, Tannin, Naphtalin.

Reaction. Normally acid, due to NaH_2PO_4; after a meal may be alkaline, but the mixed urine for twenty-four hours should be acid.

Alkalinity of freshly voided urine may be due to carbonate or phosphate of alkali-metals (Na_2HPO_4) or to the fermentation of urea in the bladder, with the formation of ammonium carbonate.

Normal urine upon keeping will also become alkaline, due to this fermentation.

Odor. Normally aromatic. The administration of essential oils and resinous drugs frequently causes characteristic odors.

Normal urine upon keeping develops an ammoniacal odor.

Urine containing blood or pus becomes putrid, evolving H_2S.

Transparency. Clear, if normal and freshly voided; after standing for a few hours forms a deposit of mucus.

If milky, due to fats or pus.

A heavy, pulverulent, buff or fawn-colored deposit, soluble upon heating, is due to Urates. Normal urine after several days' keeping deposits the greater portion of its uric acid as Acid Sodium Urate (the reaction of the urine still being acid).

A flocculent deposit from alkaline urine, insoluble upon heating, is due to Earthy Phosphates; after prolonged keeping, normal urine becomes alkaline and deposits earthy-phosphates.

Specific Gravity. $(H_2O = 1000.)$ Normal, 1015 to 1025, average for twenty-four hours, 1020; after exercise may reach 1035; after excessive drinking may drop to 1002. Diabetic urine usually exceeds 1030, and has been found as high as 1074.

Total Solids. Can be approximated by multiplying the specific gravity above 1000 by 2.33 and the number of cubic centimeters voided in twenty-four hours, and dividing the product by 1000: This gives the number of grams of solids excreted by the kidneys in twenty-four hours.

These solids average from 60 to 72 grams, and are composed as follows:

Cl, 7.50 to 9.10; SO_3, 2.00; P_2O_5, 2.50 to 3.00; HNO_3, less than 0.10; Na, 5.90 to 11.09; K, 2.50; NH_3, 0.70 to 0.77; Ca, 0.21 to 0.26; Mg, 0.21 to 0.30; Fe, less than 0.01.

Urea, 30 to 33; Uric Acid, 0.55 to 0.70; Creatinine, 0.91 to 1.00; Hippuric Acid, 0.40 to 0.70; Pigments and other organic constituents, 2.6 to 10.00.

The analysis of urine should be made, whenever possible, with a specimen representing the mixed excretions for twenty-four hours; only by doing so, will the physician be enabled to judge of the progress of the disease. In some cases the substance to be sought for is most likely to be present in urine voided at certain periods of the day; thus *Albumin* in the early morning urine; *Sugar*, after having partaken of a hearty meal consisting, in part, of starch-containing foods.

Tests for Albumin.

If the urine shows no distinct acid reaction when a piece of blue litmus paper is dipped for an instant into the sample, add $H\bar{A}$, drop by drop, until such a reaction is noted, and filter to obtain the urine perfectly transparent; if this cannot be done by filtering, add a little infusorial earth, shake well and filter, pouring small portions at a time upon the filter. With the clarified urine make the following tests:

Heat Test. Place some of the urine in a test-tube and boil the *upper portion* over a small flame; the lower cold portion by contrast will show if the boiled portion has become more or less turbid, due to the coagulation of the albumin.

Earthy Phosphates and *Resin Acids* may cause turbidity in this test, the former being soluble upon the addition of a few drops of $H\bar{A}$; the latter insoluble in $H\bar{A}$, but soluble upon the addition of alcohol.

Heller's Test. Place 5 cubic centimeters of concentrated HNO_3 in a test-tube and float about the same quantity of urine upon it so as to form a distinct layer: Albumin causes a turbid zone at the juncture of the two liquids. Minute quantities of albumin may not show until after the test has stood for half an hour. Colored rings near the juncture are due to pigments, and do not indicate albumin unless the turbid zone is noted.

Uric Acid and *Urea* in concentrated urines may cause precipitations, see page 48.

Resin Acids simulate the albumin test, but by carefully adding alcohol and mixing with the urine layer the precipitate due to these will dissolve.

Phosphates, *Alkaloids* and *Peptones* will not respond to this test.

Acidulated Brine Test. Use Acidulated Brine instead of HNO_3 and proceed as in Heller's test.

Tanret's Test. Place reagent in a test-tube and float the urine upon it: Albumin is indicated by a white turbid zone.

Peptones, *Alkaloids* and *Resin Acids* also respond; all are soluble upon heating, and the last two also upon addition of alcohol.

Picric Acid Test. Place urine in a test-tube and float the Picric Acid solution upon it: Albumin causes a white turbid zone.

Peptones, *Urates*, *Alkaloids* and *Resin Acids* also respond; all are soluble upon heating, and the last two also by addition of alcohol.

Ferrocyanide Test. Place 1 cubic centimeter $H\bar{A}$ in a test-tube, add 3 cubic centimeters $K_4Fe(CN)_6$ (5 per cent.) mix thoroughly and float the urine upon the mixture: Albumin causes a white turbid zone.

Not interfered with by *Phosphates*, *Peptones*, *Alkaloids*, *Urates* or *Resin Acids*.

Sulphocyanate Test. Mix 1 cubic centimeter $H\bar{A}$ and 5 cubic centimeters KCNS (10 per cent.) and float the urine upon it: Albumin causes a white turbid zone.

Tests for Peptones.

Slightly acidulate the urine with $H\bar{A}$ and saturate with solid $(NH_4)_2SO_4$, which precipitates *Albumin, Globulin*, *Proto-albumose*, *Hetero-albumose*, *Deutero-albumose*, filter and test filtrate by:

Tanret's Test. Float reagent upon the urine: White zone.

Picric Acid Test. Float reagent upon the urine: White zone.

Biuret Test. Make alkaline with NaOH and add a few drops $CuSO_4$ solution (2 per cent.): *Peptones* cause a pink or rose-colored solution, seen better after filtering.

Tests for Sugar (Dextrose).

The tests usually employed for the detection of dextrose are dependent upon the reducing power of this substance, in presence of alkalies, upon salts of Cu, Bi and Hg, with precipitation of Cu_2O, Bi and Hg respectively; as all three of these metals give dark colored sulphides, the presence of sulphur-containing bodies as Albumin, Cystin, etc., etc., which by boiling with alkalies yield sulphides, must be excluded.

The presence of excessive quantities of some normal urinary constituents as *Uric Acid*, *Hippuric Acid*, *Creatinine*, *Xanthine*, *Ammonia*, etc., etc., may cause interference, either by reducing the above reagents or, in presence of dextrose, by preventing the precipitation of the reduced reagent.

The administration of many drugs results in the excretion through the kidneys of substances having marked reducing power upon the above salts, thus: Acetaldehyde, Acetanilid, Alkaloids (Morphine especially), Antipyrine, Arbutin, Chloral, Chloroform, Phenacetine, Phenol, Resorcin, Rhubarb, Saccharin, Salicylic Acid, Salol, Sulphonal, Tannin, Turpentine, Trional, Urethane, etc., etc. Most of these are voided as conjugated glycuronates, to which the reducing power is ascribed. It is, therefore, important to make inquiry as to what medicinal substances had been administered, and not to depend upon a single test for dextrose.

Before making the tests the urine must be prepared, so as to remove as many of the interfering substances as possible: Boil 10 cubic centimeters of the urine, add 5 cubic centimeters hot $Pb\bar{A}_2$ mix and filter, remove excess of Pb from the filtrate by adding 5 cubic centimeters Na_2HPO_4 and again filter; with this filtrate, which is free from *Albumin*, *Uric Acid* and *Xanthine*, make the following tests:

Fehling's Test. Boil 6 cubic centimeters Fehling's solution and, if no red precipitate (Cu_2O) forms, add 3 cubic centimeters of the prepared urine and boil for two minutes: A red precipitate of Cu_2O forms in presence of Dextrose.

$BiONO_3$ Test. Mix equal quantities of prepared urine and NaOH, filter if necessary, add a minute quantity of $BiONO_3$ to the filtrate and boil for 2 to 5 minutes: A brown or black coloration due to separation of black or gray Bi indicates Dextrose.

Nylander's Test. Boil 5 cubic centimeters of prepared urine with 0.5 cubic centimeter Nylander's solution for two to five minutes: indication as above. A blank test using H_2O instead of urine should be made to see if the reagent is trustworthy.

In the following tests the method of preparing the urine is indicated as part of the test, if preparation of the urine is necessary.

Modified Fehling's Test. 5 cubic centimeters urine are boiled and, regardless of any precipitate that may be produced, mixed with 5 cubic centimeters solution **A** of Fehling's solution, which precipitates *Albumin*, *Uric Acid*, *Xanthine*, *Hypoxanthine*, *Phosphates* and *Creatinine*; allow to cool somewhat and, to make the precipitation more complete, add 0.5 to 1.0 gram crystallized Sodium Acetate and 1 drop $H\bar{A}$, dissolve and filter. To 4 cubic centimeters of the filtrate add 2 cubic centimeters more of solution **A** and 4 cubic centimeters solution **B** of Fehling's solution, and boil for two minutes; if more than 0.25 per cent. dextrose is present red Cu_2O separates before the boiling point is reached, if smaller quantities are present the separation occurs during the cooling.

Safranine Test. 2 cubic centimeters each of urine, NaOH, and Safranine solution are mixed and heated until the mixture boils freely, avoiding unnecessary agitation; if the urine contain 0.1 per cent or more of dextrose the red color will be discharged; if it contain less it will be but partially discharged. In the former case, repetition of the test, using more Safranine solution enables an approximate estimation of the dextrose to be made, as every additional 2 cubic centimeters reagent decolorized corresponds to an additional 0.1 per cent. Dextrose. Does not respond with *Uric Acid*, *Creatinine*, *Chloral*, *Chloroform*, H_2O_2 and *Hydroxylamine*, and but slowly with *Albumin*.

Phenyl-hydrazine Test. 10 cubic centimeters urine are boiled and treated with $Pb\bar{A}_2$ until precipitation is complete; boil and filter. To filtrate add NaOH to redissolve the precipitate which first forms, and then add as much Phenyl-hydrazine Hydrochlorate as will lie on the point of a pen-knife; boil for several minutes and strongly acidulate with $H\bar{A}$: a yellow turbidity or precipitate (Phenyl-glucosazone), either at once or upon standing, which melts at 204 to 205°C indicates Dextrose. (This test will detect 0.005 per cent.)

Glycuronic Acid is the only substance likely to interfere, by giving a resinous precipitate or yellow crystalline needles, melting at 150° C.

Fermentation Test. Not interfered with by all previously mentioned substances, but may be by *Levulose* and by *Glucosides.*

Fit three test tubes, each holding about 50 cubic centimeters, with stoppers through which pass glass tubes bent twice at right angles, so as to form a short arm passing through the stopper and a longer arm which extends along side of the test tube.

To 50 cubic centimeters urine, or a quantity somewhat in excess of that needed to completely fill the test tube, add 0.25 gram Tartaric Acid, and about one-sixth of a compressed yeast cake, stir to disintegrate the yeast and fill one of the test tubes with the mixture; adjust the short arm of the glass-tubing so as to be flush with the lower surface of the cork and insert cork into the test-tube, so that the excess of the liquid will be forced into the glass tubing; allow all air-bubbles to enter the glass tubing by inclining the test-tube, and then by inverting the test-tube to pass out through the longer arm; force the tubing through the cork so that it projects 2 to 3 centimeters into the test-tube, which allows the yeast to settle near the cork and prevents it from being forced out through the glass-tubing as the fermentation proceeds.

In the same manner prepare a blank test in which H_2O is used instead of the urine, and for the third tube use a 0.25 per cent. dextrose solution instead of the urine.

After one and one-half to two hours the fermentation will start and CO_2 will collect in the test-tube; the fermentation proceeds best at 25°C., and requires eighteen to twenty-four hours for its completion. To prove the production of alcohol in this test the mixture can be filtered, distilled and in a portion of the distillate the Iodoform test made, as given under Acetone.

Tests for Aceto-acetic Acid.

This, like *Acetone* and *Hydroxy-butyric Acid*, is frequently found in diabetic urine. Acidulate some of the urine with a drop or two of $H\bar{A}$ and add a few drops Fe_2Cl_6; filter to remove phosphates and add a few drops more of Fe_2Cl_6: A violet or claret color, destroyed by boiling, indicates Aceto-acetic Acid. Boiled urine will not give this test.

Antipyrin, *Phenol* and *Salicylic Acid* give similar colors, but these are not destroyed by boiling.

A urine giving the above test, upon distillation gives a distillate containing Acetone (and Alcohol, if ethyl aceto-acetate was present).

As Aceto-acetic Acid rapidly decomposes, the urine should be tested as soon as possible.

Hydroxy-butyric Acid also gives the Fe_2Cl_6 test.

Tests for Acetone.

The tests for Acetone made directly in the urine are not reliable in the presence of *Aldehyde*, *Alcohol*, *Ethers*, *Dextrose* and other *Reducing Sugars*, *Turpentine*, etc. Mix 200 cubic centimeters of urine with 3 cubic centimeters $H\bar{A}$ and distil; collect the first 40 cubic centimeters of distillate, to which add 1 cubic centimeter of dilute H_2SO_4, again distil and collect the first 20 cubic centimeters, with which make the following tests:

Fehling's Test. Upon boiling with Fehling's Solution gives red precipitate of Cu_2O.

Fuchsine=Aldehyde Test. Mix equal parts of distillate and reagent: Red color.

Iodoform Test. To 5 cubic centimeters of the distillate add 1 cubic centimeter NaOH, warm to 50°–60° C., add Iodine solution to produce a yellow color and carefully decolorize by adding NaOH: A yellowish turbidity and odor due to formation of Iodoform.

All of the above tests are also given by Aldehyde and Aceto-acetic Acid; the last one by Alcohol, Ethers, Turpentine, etc.

Nitro=prusside Test. To a few cubic centimeters add a piece of Nitro-prusside Test-paper and make alkaline with NaOH: A ruby color is produced which, upon acidifying with $H\bar{A}$, changes to a carmine or purple-red and after some time to violet, and finally blue.

Tests for Urea.

Most readily identified by a microscopic examination of the nitrate or oxalate, produced by adding nitric or oxalic acid to the urine, and concentrating to allow crystallization. In concentrated urines large tabular plates of urea nitrate are frequently obtained in making **Heller's Albumin Test.**

Alkaline Hypobromites or **Hypochlorites** decompose urea liberating N to the extent of 92 to 93 per cent. of the theoretical yield; the loss being due to the formation of cyanate; 0.100 gram gives about 38 cubic centimeters of moist N at 18° C.

Biuret Test. A few small crystals of urea or one of its salts heated to perfect fusion in a dry test-tube and until the odor of NH_3 is no longer discernible, leaves a residue which, dissolved in a small quantity of H_2O and made alkaline with NaOH, gives with a few drops of $CuSO_4$ a red color, and upon further addition of $CuSO_4$ a red-violet, and finally blue-violet color.

Tests for Uric Acid.

HCl or **HNO_3** causes precipitation of Uric Acid from urates; in **Heller's Albumin Test** this is frequently noticed in concentrated urines, the precipitate, however, does not form at the line of juncture, but some distance above in the layer of urine.

NH_4Cl (solid) added to saturation and allowed to stand for two hours (in quantitative analysis) causes complete precipitation as Acid Ammonium Urate.

Fehling's Solution is reduced upon boiling.

Murexide Test. Add a few drops of HNO_3 to a small quantity of urine and carefully evaporate to dryness over a small flame; exposing the residue to the vapor of NH_3 produces a purple color due to the formation of Murexide or Ammonium Purpurate.

Tests for Pigments.

Urobilin. Present in normal urine, but in abnormal quantities may be the cause of a red color.

1. Add to 10 cubic centimeters urine a few drops $ZnCl_2$ (10 per cent.) and then NH_4OH until the precipitate redissolves upon agitation: the solution will show a fine green fluorescence.
2. 20 cubic centimeters urine are mixed with 2 cubic centimeters saturated $CuSO_4$ solution, and this mixture saturated with solid $(NH_4)_2SO_4$; then add 10 cubic centimeters $CHCl_3$ and shake for five to ten minutes: the $CHCl_3$ solution will show a copper-red color.

Bile-pigments. Not present in normal urine; cause yellowish-green, green, greenish-brown or almost black color.

1. Stain linen or filter-paper yellow; if the yellow stain on filter-paper be touched with a drop of HNO_3, containing a trace of HNO_2, the edge of the spot will be colored violet or blue, the center emerald-green.
2. Fuming HNO_3 (HNO_3 + trace HNO_2) placed in a test-tube and the urine floated upon it will show a green ring at line of contact and below this violet, red and yellow zones. The green color alone is characteristic, but may also be caused by Antipyrine.
3. A dilute Iodine or Bromine solution floated upon the urine will cause a grass-green ring. Antipyrine also gives this test.
4. Almost neutralize 30 cubic centimeters urine with Na_2CO_3 and add 10 cubic centimeters $Zn\bar{A}_2$ (20 per cent); collect voluminous precipitate, wash with H_2O and treat with a little NH_4OH; the filtrate will show a blue fluorescence.
5. 100 to 200 cubic centimeters urine are made alkaline with Na_2CO_3 and precipitated by $BaCl_2$; the precipitate which is yellow in presence of bile-pigments, yields its color to boiling alcohol containing a few drops of H_2SO_4, forming a fine green colored solution. If this solution be diluted with an equal volume of H_2O and shaken with 5 cubic centimeters $CHCl_3$ the latter will be colored deep green.
6. Bilirubin, the main biliary pigment, is extracted from acidulated urine by $CHCl_3$ (but not in presence of $CuSO_4$); the $CHCl_3$ solution evaporated gives a residue soluble in NaOH, which by exposure to air turns green.

Blood-pigments are always accompanied by Albumin.

1. Make the urine strongly alkaline with NaOH and boil: Bottle-green coloration and brown-red precipitate of earthy phosphates colored by blood.
2. Make the urine slightly alkaline with NaOH, and then acidify with Tannic Acid dissolved in $H\bar{A}$: A dark-brown precipitate of Hæmoglobin Tannate.
3. Boil the urine and add a trace of HNO_3: Coagulated Albumin in presence of blood will have a more or less brown color.

Indican (Indoxyl-Potassium Sulphate.)

1. Mix 4 cubic centimeters concentrated HCl and 2 cubic centimeters urine: Blue or violet color indicates excess of Indican.
2. To 10 cubic centimeters urine and 10 cubic centimeters HCl add 2 to 3 cubic centimeters $CHCl_3$ and then NaClO or Cl water or Fe_2Cl_6: Blue or violet color. The NaClO or Cl water must be added drop by drop to avoid excess, which destroys the color; Fe_2Cl_6 in excess does not destroy the color.
3. Boil a mixture of 10 cubic centimeters each of urine and HCl after adding a few drops of HNO_3; then cool and agitate with a small quantity of $CHCl_3$: Blue or violet color.

Pus is always accompanied by Albumin.

Allow deposit in the urine to settle, decant the supernatant liquid and treat the deposit with KOH: A glairy, gelatinous mass, sticking to the sides of the container.
Because of the presence of Albumin, a cloudiness due to pus increases upon heating, while Urates dissolve; addition of HNO_3 also increases the cloudiness, while earthy phosphates dissolve.

The Diazo-Reaction in urine is most commonly obtained in typhoid fever (from the fourth to the seventh day and thereafter) and occasionally in pulmonary and miliary tuberculosis, in measles, scarlet fever, erysipelas and pyæmia.

For the test two solutions are necessary : **A,** 2 grams Sulphanilic Acid dissolved in 50 cubic centimeters HCl and 1,000 cubic centimeters H_2O ; **B,** 0·5 gram Sodium Nitrite dissolved in 100 cubic centimeters H_2O.

To make the test mix 50 parts A with 1 part B ; equal parts of this mixture and of urine are made strongly alkaline with NH_4OH and shaken in a test-tube. For a positive test it is not sufficient to produce a distinct red-colored solution, but upon shaking, the *foam must* show a distinct red color.

Urinary Concretions.

Heat a portion of the powdered material upon platinum foil or a porcelain crucible lid:

A. 1. Burn without flame, giving odor of HCN and leaving but a slight residue:

a. Give Murexide Test: **Uric Acid, Ammonium Urate** (**K** or **Na Urate** leaves an alkaline residue, effervescing with HCl); distinguished by tests for NH_4, K and Na; only the first one is insoluble in boiling H_2O.

b. Does not give Murexide Test, but gives a yellow residue after evaporating with HNO_3, not changing with NH_4OH, but becoming red with KOH: **Xanthine.**

2. Burn with flame, leaving but a slight residue:

a. Pale blue flame, odor of SO_2: **Cystin,** soluble in NH_4OH giving six-sided plates upon slow evaporation, and black PbS when boiled with $Pb\bar{A}_2$ and KOH.

b. Yellow flame.

aa. Odor of Shellac or Benzoin: **Urostealith** (fat and Ca and Mg salts of fat acids), soluble in alcohol and ether.

bb. Odor of burnt feathers: **Fibrin,** insoluble in alcohol and ether, soluble in KOH.

c. Purplish-red vapors, condensing to a dark blue sublimate: **Indigo,** soluble in $CHCl_3$.

B. Do not burn, but leave a considerable quantity of residue after ignition:

1. Residue effervesces with HCl:

a. Give Murexide Test: **K** or **Na Urate.**

b. Do not give Murexide Test: $\mathbf{CaCO_3}$, $\mathbf{CaC_2O_4}$.

2. Original material effervesces with HCl: $\mathbf{CaCO_3}$.

3. Give test for H_3PO_4; original material heated with KOH:

a. Odor of NH_3: $\mathbf{MgNH_4PO_4}$.

b. No odor of NH_3: $\mathbf{Ca_3(PO_4)_2}$ or $\mathbf{Mg_3(PO_4)_2}$.

Mixed Concretions are frequent as: **Uric Acid** and $\mathbf{CaC_2O_4}$; **Carbonates** and **Phosphates** of **Ca** and **Mg** with $\mathbf{CaC_2O_4}$ and **Ammonium Urate.** In these a qualitative analysis for acids and bases must be made after the above scheme has been followed.

Urinary Sediments can be examined according to the above scheme but, are best examined under the microscope for structure, solubilities and special tests.

Reagents.

Unless otherwise stated, the weights given are for 100 cubic centimeters Reagent.

Acidulated Brine. See $NaCl + HCl$.

$AgNO_3$. 0.5 grams.

Alcohol, Ethyl. (C_2H_5OH or C_2H_6O.) 95 per cent.

Alcohol, Methyl. (CH_3OH.) 95 per cent.

Alkaline Hypobromite for Urea. To 25 cubic centimeters NaOH solution (10 grams in 25 cubic centimeters) add 2.5 cubic centimeters Bromine; prepare when needed.

Aqua Regiae. 4 vols. HCl (1.12), 1 vol. HNO_3 (1.20).

$BaCl_2$ $2H_2O$. 5 grams.

Bismuth, Alkaline Solution (Nylander's Solution). 10 grams Rochelle Salt, dissolved in 250 cubic centimeters NaOH solution (10 per cent), warm and dissolve in this 5 grams $BiONO_3$ H_2O.

$CaCl_2$. 5 grams.

Cl Water, *for qualitative testing.* 1 gram $CaOCl_2$, mixed with 75 cubic centimeters H_2O, dissolved by the addition of 5 cubic centimeters HCl (1.12). *Use only in acid solutions.*

$CHCl_3$ (U.S.P).

$CuSO_4$ $5H_2O$. 2 grams.

Copper, Alkaline Solution (Fehling's Solution).

A. 6.928 grams $CuSO_4$ $5H_2O$, dissolved in H_2O to make 100 cubic centimeters.

B. 34.6 grams Rochelle Salt and 18 grams NaOH (90 per cent.) dissolved in H_2O to make 100 cubic centimeters. *For use, mix equal volumes of the two solutions.*

Diazo-Reagents. See page 50.

Fehling's Solution. See Copper, Alkaline Solution.

Fe. Card Teeth.

Fe_2Cl_6. Anhydrous. 2 grams.

$FeSO_4 + H_2SO_4$. 5 grams $FeSO_4$ $7H_2O$, dissolved in 20 cubic centimeters dil. H_2SO_4 and H_2O to make 100 cubic centimeters.

Fuchsine Solution (Magenta Solution.) 0.1 gram.

Fuchsine-Aldehyde Reagent. To 30 cubic centimeters Fuchsine Solution add 20 cubic centimeters $NaHSO_3$ solution (sp. gr. 1.31) and dilute with a mixture of 3 cubic centimeters concentrated H_2SO_4 and 200 cubic centimeters H_2O; the red color is discharged in a short time, when it is ready for use.

Gelatin Solution. 1 gram Gelatin dissolved in 100 cubic centimeters hot H_2O, mixed with 66 cubic centimeters glycerin and diluted with H_2O to make 200 cubic centimeters; lastly add 4 drops Oil of Cassia as a preservative.

$H\bar{A}$ or **$HC_2H_3O_2$.** 10 grams.
Dilute 24 cubic centimeters $H\bar{A}$ (U.S.P.) with H_2O to make 90 cubic centimeters.

HCl (sp. gr. 1.12). 25 grams.
Dilute 70 cubic centimeters HCl (U.S.P.) with H_2O to make 100 cubic centimeters.

HCl dilute. 5 grams.
Dilute 14 cubic centimeters HCl (U.S.P.) with H_2O to make 100 cubic centimeters.

HNO_3. (Sp. gr. 1.42; U.S.P.) 98·3 grams.

HNO_3 (sp. gr. 1.20). 40 grams.
Dilute 40 cubic centimeters HNO_3 (U.S.P.) with H_2O to make 100 cubic centimeters.

HNO_3 dilute. 10 grams.
Dilute 10 cubic centimeters HNO_3 (U.S.P.) with H_2O to make 100 cubic centimeters.

HNO_3, fuming. Concentrated HNO_3, containing some lower oxides of Nitrogen; for reagent in urinalysis 1.5 grams $NaNO_2$, dissolved in 100 cubic centimeters HNO_3 (sp. gr. 1.42) will answer.

H_2S. Generated by action of dilute H_2SO_4 upon FeS.

H_2SO_4 concentrated (sp. gr. 1.835) 169,5 grams.

H_2SO_4 dilute. 10 grams.
Dilute 5 cubic centimeters H_2SO_4 (U.S.P.) with H_2O to make 80 cubic centimeters.

$HgCl_2$. 2 grams.

HgI_2 2KI or K_2HgI_4 (Potassio-mercuric Iodide, Mayer's Reagent, Potassium Iodo-Hydrargyrate): Dissolve 1.354 grams $HgCl_2$ in 60 cubic centimeters H_2O, and add solution of 4.980 grams KI in 10 cubic centimeters H_2O; lastly dilute with H_2O to 100 cubic centimeters.

HgI_2 2KI + $H\bar{A}$ (Tanret's Reagent). 1.35 grams $HgCl_2$, 3.32 grams KI, 50 cubic centimeters $H\bar{A}$ (10 per cent.) and H_2O to make 100 cubic centimeters.

Iodine Solution. 1.27 grams I and 1.8 grams KI.

KCN. 5 grams.

KCNS. *For qualitative tests.* 2 grams.
For Albumin tests. 10 grams.

K_2CrO_4. 5 grams.

$K_4Fe(CN)_6$ $3H_2O$ for *Fe(ic) tests.* 2 grams.
For Albumin tests. 5 grams.

$K_6Fe_2(CN)_{12}$ freshly made. 2 grams.

KI. 1 gram.

KOH. 5 grams.

Labarraque's Solution. See NaClO + NaCl.

Magenta Solution. See Fuchsine Solution.

Magnesia Mixture. 10 grams $MgSO_4$ $7H_2O$ and 20 grams NH_4Cl are dissolved in 80 cubic centimeters H_2O and 42 cubic centimeters NH_4OH (10 per cent. NH_3) added; allow to stand several days and filter.

For qualitative testing, dilute 25 cubic centimeters of above solution with 50 cubic centimeters H_2O, and add 25 cubic centimeters NH_4OH (10 per cent. NH_3).

Mayer's Reagent. See HgI_2 2KI.

NaCl + HCl (Acidulated Brine). Mix 100 cubic centimeters saturated NaCl solution with 10 cubic centimeters HCl (1.12); allow to stand for several hours and filter.

NaClO + NaCl (Labarraque's Solution). 7.5 grams $CaOCl_2$ and 15 grams $Na_2CO_3 10H_2O$ are triturated with 100 cubic centimeters H_2O, allowed to stand twenty-four hours and strained.

Na_2CO_3 $10H_2O$. 5 grams.

Na_2HPO_4 $12H_2O$. 5 grams.

NaOH. 5 grams.

Na_2S. Dissolve 10 grams NaOH in H_2O to make 100 cubic centimeters. Saturate 50 cubic centimeters of this with H_2S and add the remaining 50 cubic centimeters.

$Na_2S_2O_3$ $5H_2O$. 1 gram.

$(NH_4)_2CO_3$. Dissolve 10 grams Ammonium Carbonate in 11 cubic centimeters NH_4OH (10 per cent NH_3) and H_2O to make 100 cubic centimeters.

$(NH_4)_2C_2O_4$. 5 grams.

NH_4Cl. 5 grams.

$(NH_4)_2MoO_4$. Dissolve 5 grams $(NH_4)_2MoO_4$ in 32 cubic centimeters H_2O and pour into 32 cubic centimeters HNO_3 (1.20); add 4 grams NH_4NO_3 and 2.5 grams $H_2C_4H_4O_6$, and dilute with H_2O to 80 cubic centimeters.

For qualitative testing, mix 20 cubic centimeters of above solution with 10 cubic centimeters HNO_3 (1.20), add 5 grams NH_4NO_3 and dilute with H_2O to make 100 cubic centimeters.

NH_4OH. 10 grams NH_3.

NH_4OH dilute. 5 grams NH_3.

$(NH_4)_2HPO_4$. 5 grams.

Nylander's Solution. See Bismuth, Alkaline Solution,

$Pb(C_2H_3O_2)_2$ $3H_2O$ or $Pb\bar{A}_2$. 5 grams.

Pb_3O_4 (Red Lead). Should give no test for Mn when heated with dil. HNO_3. See **Dppp.**

Picric Acid. Saturated H_2O solution.

Potassio-mercuric Iodide. See HgI_2 2KI.

Potassium Iodohydrargyrate. See HgI_2 2KI.

$PtCl_4$. 5 grams.

Safranine Solution. 0.1 gram.

Sn. Pure Tin-foil cut into small squares.

$SnCl_2$ $2H_2O$. 4 grams $SnCl_2$ $2H_2O$ dissolved in 25 cubic centimeters HCl (1.12) and diluted with H_2O to make 100 cubic centimeters. Keep some Sn in bottle to prevent oxidation.

Starch Solution. Mix 1 gram starch with H_2O to make a smooth paste and pour slowly into 100 cubic centimeters boiling H_2O; boil until thoroughly gelatinized, cool, add 0.4 cubic centimeter Oil of Cassia and dilute to 200 cubic centimeters.

Tannic Acid + $H\bar{A}$ for Blood-pigments. 2 grams Tannic Acid, 10 cubic centimeters $H\bar{A}$ (10 per cent.), 20 cubic centimeters alcohol and H_2O to make 100 cubic centimeters.

Tanret's Reagent. See HgI_2 2KI + $H\bar{A}$.

Test Papers. Dip strips of unsized paper into solutions of reagents of stated strength, allow to dry and cut into pieces of usual size.

Indigo. 0.6 gram Indigo-carmine in 100 cubic centimeters H_2O.

Lead Acetate (PbA_2). 5 grams.

Nitro-prusside (of Sodium). 10 grams $Na_2FeNO(CN)_5\ 2H_2O$.

Starch. 2 grams.

Starch + KI. 2 grams starch, 0.5 gram KI.

Starch + KIO_3. 2 grams starch, 0.5 gram KIO_3.

Turmeric. 15 grams ground Turmeric are macerated for twenty-four hours with 60 cubic centimeters H_2O, placed in a small percolator, and extracted with H_2O until a portion of the percolate made alkaline with KOH ceases to give any red coloration; throw away the percolate. Dry the insoluble portion at a low temperature, macerate for three days with 90 cubic centimeters alcohol and filter; use filtrate for saturating the paper.

$Zn(C_2H_3O_2)_2\ 2H_2O$ or $Zn\overline{A}_2$. 20 grams; or 26.5 grams $ZnSO_4\ 7H_2O$, 25 grams $Na\overline{A}$ and H_2O to make 100 cubic centimeters.

$ZnCl_2$. 10 grams; or dilute 13 cubic centimeters U.S.P. solution (50 per cent.) with H_2O to make 100 cubic centimeters.

$ZnSO_4\ 7H_2O$. 1 gram.

Errata.

Page 8. Under **B** 1 read $MgO + 2HNO_3 = Mg(NO_3)_2 + H_2O$.
B 7 read $Na_4As_2O_7 + H_2O = 2Na_2HAsO_4$.
Page 9. Under **B** 9 read $Cr_2Cl_6 + 3(NH_4)_2S + 6H_2O =$
Page 19. Top line between **Cr_2** and **Mn** read **Al_2**
Page 23. Sixth line from top read (10 per cent.).
Page 26. Read **Epf.** Add 5 cubic centimeters.
Page 27. Fourth line from top read $Mg_3(PO_4)_2$.

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